VOL. XVII. [JANUARY, 1895.] NO. 1.

AMERICAN CHEMICAL JOURNAL.

Contributions from the Laboratory of General Chemistry, University of Michigan.

I. ON THE ACTION OF CHLORCARBONIC ESTER ON SODIUM ACETONE.

BY PAUL C. FREER.

Some time ago I published a short preliminary notice[1] on this subject (in conjunction with Geo. O. Higley). In this paper we demonstrated that a neutral oil which, on distillation, could be separated into two portions (one boiling between 125° and 135° and one above 200°) is to be obtained as a product of the reaction. At that time we isolated from the lower fraction, a colorless fluid, with a boiling-point of approximately 130°, and as the analyses, as well as the vapor density determinations of this body gave us numbers which agreed very well with those calculated for aceto-acetic ester, and as, furthermore, it did not react with phenylhydrazine and yielded carbon dioxide, acetone, and alcohol on saponification, we felt justified in assuming that the substance in question had a constitution to be expressed by the formula

$$\begin{matrix} CH_3.COCO_2C_2H_5 \\ \| \\ CH_2 \end{matrix} ;$$

[1] This Journal, 13, 322.

There was one circumstance, mentioned at the time in connection with this work, which seemed to demand further investigation, and this was the fact that, although the numbers obtained for carbon agreed perfectly with the theory, the hydrogen was always found to be somewhat too high. It was with the purpose of finding an explanation of this discrepancy that I resumed the research with the larger quantities of sodium acetone, and the better apparatus which were subsequently at my disposal, and, in so doing, I discovered that the previously described oil, with a boiling-point of 130°, was in reality a mixture of several bodies, all of which distill at about the same temperature. It is impossible to accomplish the perfect separation of these bodies by fractional distillation, yet such a mixture would give analytical results in accordance with those detailed in the previous preliminary notice.

One fact, however, definitely appears as a result of the new experimental work, and this is that the greater portion of the various bodies which are obtainable as a result of the reaction between sodium acetone and chlorcarbonic ester is in reality the carbonic ester, the existence of which was previously assumed, and to which the formula $CH_3.COCO_2C_2H_5$ had

$$CH_3$$

been assigned. Furthermore, it has never been possible to isolate either aceto-acetic ester, or the products of the reactions between the sodium derivative of the latter body and chlorcarbonic ester (acet-malonic ester or methin-tricarboxylic ester) from the substances which are produced,[1] so that no proof is obtainable that addition-products, in which the substituting radicle is attached to carbon, are here formed, (as is the case in the action of benzoyl chloride on sodium acetone). The behavior of this body toward chlorcarbonic ester, therefore, furnishes definite proof that the sodium in sodium acetone is

[1] Once only could I obtain from the higher-boiling portions of the products of the reaction an oil which gave a violet coloration with ferric chloride. As I suspected the presence of aceto-acetic ester, I extracted with ten per cent. sodium hydroxide solution, neutralized the extract at once, and then shook the resulting fluid out repeatedly with pure ether. On evaporating the solvent, only traces of an oil (which colored ferric chloride), remained. This substance was too small in quantity to permit of identification, but it most probably was aceto-acetic ester.

joined to oxygen only. It follows from the above, however, that the mono- and dibenzoyl-acetone (which I formerly obtained by the action of sodium acetone on benzoyl chloride) were derived from intermediary addition-products, as I assumed in my paper on that subject.[1] The only other view which was in accord with the facts previously observed was that *two* sodium derivatives of acetone existed, with the following structures:

I. $CH_3.CO.CNaH_2$ and II. $CH_3.CONa:CH_2$.

Of these the first would give C, the second O substitution products when treated with organic halides. This interpretation of the facts is now definitely contradicted by the behavior of sodium acetone toward chlorcarbonic ester, while, at the same time, this work furnishes strong support to the theory of processes of addition, which is at the present time accepted by many chemists. As mono- and dibenzoyl acetone *must* have resulted from the decomposition of foregoing addition-products, it follows that in the case of aceto-acetic ester, the formation of C substituted bodies should also be ascribed to identical processes.

Experimental Part.

Preparation of the Initial Product.

Three grams of sodium (in the form of the finest wire) are placed in a flask, covered with absolute ether and then converted into sodium acetone, according to the method described in my former paper,[2] air being at the same time rigidly excluded by means of a current of pure hydrogen. After all of the sodium has disappeared, somewhat less than the calculated quantity of chlorcarbonic ester is gradually run in through a dropping funnel. A violent reaction begins at once, sodium chloride apparently being formed, while the process may at times become so energetic as to necessitate the cooling of the flask by means of ice-water. After all of the chlorcarbonic ester has been added, the container is tightly stoppered while a current of hydrogen is passing into it, and it is then allowed to stand in a warm place for about ten days

[1] This Journal, **15**, 604. [2] *Ibid*, **15**, 588.

By this time the white salt, which has been formed, has almost entirely settled. The latter is then filtered off, washed with absolute ether, and it, as well as the straw-colored filtrate, is preserved until the results of fifteen such processes can be worked up at the same time.

The Investigation of the Solid Product.

The solid, which separated during the above reaction, presumably was sodium chloride, and, indeed, acting on that supposition during the former work on this subject, it was thrown aside without further examination. Subsequently it occurred to me that this precipitate might not be as simple in composition as I had at first supposed, and on investigation, the analyses showed that at least 15 per cent. of the salt consisted of *sodium carbonate*, while a very small percentage (less than 2.5) was the sodium compound of an alcohol.[1] This rather surprising result shows that there must have been considerable decomposition, either of the chlorcarbonic ester used in the original reaction, or of the carbonic esters which were formed subsequently. This decomposition may be due to sodium hydroxide, which could have resulted from the action of water (formed by the condensation of acetone to phorone), in which event some free alcohol should be found among the products of the reaction; or it can have been caused by double decomposition taking place between the sodium-organic compounds and the carbonic esters which are produced:

$$2NaOR + CO_2(OR)_2 = Na_2CO_3 + 2ROR.$$

If the latter change were to have taken place, then ethyl-isoacetone ether[2] might be expected to be formed, but, heretofore, I have not been able to prove the presence of this body. This fact need not exclude the possibility of its presence, however, for such an ether would, owing to its low boiling-point (62°), be most difficult to detect in the presence of the large amount of ethyl ether which is necessary for successful work with sodium acetone. It is very likely that both of the above changes take place simultaneously, for I have been

[1] Presumably sodium isopropylate, unacted on by the chlorcarbonic ester.

[2] The derivatives of methyl-vinyl alcohol; $CH_3.COH:CH_2$ (β-allyl alcohol) may perhaps best be termed derivatives of isoacetone, a nomenclature adopted by Claisen. Ann. Chem. (Liebig), **277**, 169.

able to isolate a considerable quantity of free alcohol from the fluid products of the reaction, yet this alcohol is not of a sufficient quantity to account for all of the sodium carbonate which is produced. The presence of sodium carbonate, mixed with the salt which was formerly supposed to be sodium chloride, shows that it is possible to have had similar decompositions in other cases where chlorcarbonic ester has reacted with sodium-organic compounds (so, for example, with sodium aceto-acetic ester) so that those precipitates which heretofore have been considered as being nothing but sodium chloride, may, in reality, also contain the carbonate, while the formation of the latter body may naturally influence the entire reaction. Another possible source of the sodium carbonate may be found in the decomposition of chlorcarbonic addition-products to sodium acetone (*i. e.* aceto-acetic ester or its derivatives) and this fact may account for the entire absence of such bodies among the substances to be isolated.

The Fluid Products of the Reaction.

The straw-colored, filtered liquid was first roughly divided into two parts by distillation, one portion boiling up to 110° and the second above this point. A considerable quantity of hydrochloric acid separates during this operation, while the fluid, which remains, turns to a dark-green color.[1] I was also able to isolate a certain amount of ethyl alcohol from the

[1] The hydrochloric acid is formed only during the process of distillation. It could not have been present before, otherwise it would have decomposed the sodium carbonate. In spite of the fact that less than the theoretical quantity of chlorcarbonic ester is used during the reaction, the latter body is always to be found among the distillation products. This fact is probably due to the saponification of a certain amount of the carbonic esters which are formed. This saponification would result in the removal of a portion of the sodium and the formation of sodium carbonate. The excessive chlorcarbonic ester can now, on distillation, react with the alcohol which has been set at liberty, thus forming carbonic diethyl ester and hydrochloric acid, while the latter body adds itself to the unsaturated organic substances which are present, to be once more separated when the latter are heated. As a result, carbonic diethyl ester should be among the products of the reaction, and, indeed, as will be shown below, I have succeeded in isolating a considerable quantity of that body from the oil boiling between 125° and 135°. This formation of hydrochloric acid is of importance because the production of the condensation products of acetone is to be attributed in part to its action. Equally complicated results have also been obtained in other reactions between chlorcarbonic esters and sodium alcoholates. Röse, Ann. Chem. (Liebig), **203**, 227. Another explanation for the hydrochloric acid can be found in the decomposition of addition-products; this will be discussed subsequently.

lower fraction. This was accomplished by means of careful distillation with a dephlegmator, extraction with water of the part passing over between 68° and 85°, saturation of the solution with potassium carbonate, separation of the organic liquid, treatment with sodium bisulphite solution, etc., according to the usual methods. No isopropyl alcohol was present, as was proved by analyses which were made. The oil passing over between 85° and 110° consisted, for the most part, of unchanged chlorcarbonic ester and of the bodies belonging to the next higher fraction.

The part boiling above 110° was placed in contact with a little water, and was then allowed to stand for several hours. During this time crystals of hydrated pinacone separated in considerable quantity. The presence of free pinacone must either be attributed to reactions similar to those which produced the free ethyl alcohol; or else it is to be referred to the action of an acid, which later is formed as a result of previous processes of addition (as is the case in the work with benzoyl chloride[1]), but, as was mentioned before, addition-products or their derivatives are not to be found among the final bodies.[2] After the pinacone was filtered, the clear liquid was extracted repeatedly with a 10-per cent. sodium hydroxide solution,[3] washed several times with water, dried over calcium chloride, and then all that would pass over below 150°, distilled off.

Investigation of the Low-Boiling Oil.

The portion of the whole oil which passed over between 110° and 150° was carefully and repeatedly fractioned, and finally separated as follows:

112°–126° (contains considerable $ClCO_2C_2H_5$); 126°–128°: 8 grams; 128°–129°: 8 grams; 129°–130°: 24 grams; 130°–132°: 16 grams; 132°–137°: 8 grams.[4]

[1] This Journal, **15**, 604.

[2] The presence of sodium pinaconate among the products of the action of sodium on acetone was proven in this Journal, **15**, 592.

[3] The alkaline solution was instantly neutralized with sulphuric acid and then extracted repeatedly with pure ether. On evaporating the solvent, nothing but a few crystals of pinacone remained. Only once did I succeed in getting about 0.8 of a gram of an oil which colored ferric chloride solution and which, presumably, was aceto-acetic ester. Acid organic substances are, therefore, not formed in any quantity.

[4] The above amounts are not exact, but simply approximate.

All of these portions contained chlorine, and in consequence of this fact, they were afterwards separately distilled over small pieces of sodium until all of the halogen was removed. They were then carefully refractioned, but it was impossible to isolate a body with a perfectly constant boiling-point from any of the portions. For example, the fraction passing over between 129° and 130° would, on repeated distillation, yield a small quantity of an oil boiling between 124° and 128° as well as a few drops of a substance which would not pass over under 150°, and even if a product which, when working with larger quantities distilled within 0.5°, was refractioned by itself, no other result could be obtained.[1] Indeed, nothing else is possible under the circumstances, for this oil is, as I will demonstrate below, an inseparable mixture of several bodies, which, furthermore, interact, the one with the other, when they are heated. This fact is entirely in accord with the discovery of Röse,[2] who found that a mixture of chlorcarbonic methyl or ethyl ester, with an alcohol of higher molecular weight, was changed *even at ordinary temperatures* in such a way that the alcohol of lower molecular weight was expelled from its compounds by the one with the higher; so that for example carbonic dipropyl ester and methyl alcohol are produced from carbonic methyl propyl ester and propyl alcohol, although some of the original bodies still remained after all interaction was complete.

The product of the reaction between chlorcarbonic ester and sodium acetone, after being purified and fractioned as detailed above, is perfectly colorless and possesses a strong ethereal odor (reminding one of that of carbonic diethyl ester); it does not react with phenylhydrazine, even after standing for a number of hours, and it takes up bromine at once and in the cold, without liberating hydrobromic acid. When warmed for a short time with baryta water, or for a longer

[1] I have endeavored, by using the most varied means of purification, to obtain a product with a perfectly constant boiling-point, but without success. So, for example, I have treated the crude oil with phenylhydrazine until no further reaction could be noticed; have then distilled the mixture so obtained twice in a current of steam; and have finally fractioned this nearly pure product by the same means. I have also distilled the oil from perfectly pure phenylhydrazine, at a pressure of 30 mm., but could observe no difference in the result.

[2] Ann. Chem. (Liebig), **208**, 240.

time with hydrochloric acid, it is completely broken down into carbon dioxide, ethyl alcohol, isopropyl alcohol, and *acetone*. This oil obviously is a mixture of carbonic esters *which yields acetone on saponification*, but in order to prove that at least a portion of this acetone *must have been present* in an isoacetone carbonic ester, it is necessary experimentally to fulfill the following three conditions:

I. The combustions must yield numbers which agree with those calculated for a mixture of carbonic esters, such as the one under discussion.

II. The amount of carbon dioxide which is obtainable on saponification must be so great as to exclude the possibility of having all of the acetone derived from a compound which is not a carbonic ester of isoacetone.

III. The quantity of acetone to be regained by saponification must be so large that, after considering the foregoing conditions, the theory that this acetone may have resulted from a body which is not an ester of carbonic acid, is excluded.

As the following details prove, these three conditions have, in reality, been experimentally realized.

I. It seems unnecessary to enumerate all of the analyses which were made, because the results of a series of preparations are in practical agreement; in the following table I have compiled the averages of a considerable number of determinations:

Calculated for:	Carbon, per cent.	Hydrogen, per cent.	Oxygen, per cent.
Carbonic diethyl ester:—$C_5H_{10}O_3$	50.84	8.47	40.69
" ethyl-isoacetone ester:—$C_6H_{10}O_3$	55.38	7.69	36.93
" di-isoacetone ester:—$C_7H_{10}O_3$	59.01	7.04	33.95
" ethyl-isopropyl ester:—$C_6H_{12}O_3$	54.53	9.··	36.47
" di-isopropyl ester:—$C_7H_{14}O_3$	57.53	9.58	32.99
Found for the fractions:			
125.5° to 126.5°	53.48	8.55	37.97
129° to 130°	55.40	8.23	36.37
131° to 132°	55.35	8.93	35.72
132° to 134°	56.17	9.01	34.82
136° to 138°	57.64	9.16	33.20

An examination of the above table shows that the percentages of carbon and hydrogen increase as the boiling-point advances, yet all of the numbers are undoubtedly such as would

be obtained from a mixture of the above carbonic esters. The only other class of bodies which are possibly present in the oil under discussion (and which would not react with phenylhydrazine, while possessing the proper boiling-point) would be reduction-products or esters of mesityl oxide, and such substances would yield 20 per cent. more carbon and 4 per cent. more hydrogen than the quantities in reality obtained.[1] The analyses of the fraction 129° to 130° (when purified with the greatest care) agree quite well with the theory for carbonic ethyl-isoacetone ester (with the exception that the hydrogen is 0.6 per cent. higher than the amount calculated for such a body) and the vapor density (calculated 4.5; found 4.44) is also in accord with the view that this portion of the oil contains the expected substance in a nearly pure state.

II. As the analytical data agree with those numbers which should be obtained, the next question to be decided is whether the experimental results are also in accord with the second of the above conditions. The best method for determining the relative quantity of carbon dioxide which is present in the body under discussion, was found to be in saponification by means of baryta water. A small quantity of the oil was weighed in a glass bulb, which was drawn to a point and afterward fused at the tip. This bulb was heated to 110° in a sealed tube with a slight excess of baryta water, the reaction being complete after about one-half an hour. After opening the tube, the barium carbonate was filtered, washed with boiling water, dissolved in dilute hydrochloric acid, reprecipitated with ammonium carbonate, again filtered into a Gooch crucible and finally weighed, after drying at 120°. The quantity of carbon dioxide to be obtained varied somewhat for the different fractions. It was 32 per cent. for 128°, and 33.7 per cent for 130°–132°. All of the determinations were in practical accord. The calculated amounts of carbon dioxide are as follows:

1. For $CO(OC_2H_5)_2$; CO_2 per cent. 37.28.

[1] Some analyses vary from the numbers given above, indeed the carbon may be as high as 59 and the hydrogen as high as 10.2 per cent. The cause of this difference will be given below. A reduction-product of mesityl oxide, if decomposed by hydrochloric acid, would certainly have to yield isopropyl alcohol. The latter body is not among the saponification-products of the lower fractions.

2. For $CO(OC_2H_5)_2$; CO_2 per cent. 30.98.

3. For $CO(OC_2H_5)(OC_3H_5)$; CO_2 per cent. 33.84. (Found 33.7 per cent.)[1]

4. For $CO(OC_2H_5)(OC_3H_7)$; CO_2 per cent 30.55.

The above figures demonstrate that the quantity of carbon dioxide is also in full accord with the theory. The amount of acetone to be obtained by saponification must be very small indeed if, considering the high percentage of carbon dioxide, it is to be present in any other form than as a carbonic ester of isoacetone. As will be seen from the above numbers, the experimental data agree best with the body (3) which was theoretically expected to be present. Indeed one would be justified, after taking all of the previous work into consideration, in assuming its existence as a pure chemical individual in the fraction from 130° to 132°; nevertheless it is also possible that we have here a mixture (for example of 1, 2, and 4, etc.) which would give the same analytical results. It is therefore necessary to bring further proof to bear on the subject, and, if possible, to fulfill the third of the above conditions.

III. In order to ascertain the percentage of acetone which is obtainable from the oil in question, the most convenient method was found to be in saponification by means of dilute hydrochloric acid, and subsequent isolation of the organic bodies produced. About 15 grams of the oil (boiling-point 128°) were boiled for ten hours with an excess of 20-per cent. hydrochloric acid, with an inverted condenser the outer end of which was connected with a wash-bottle containing a little water, so as to prevent any possible escape of organic fluids. At the expiration of the above-mentioned time, the small quantity of unchanged oil was separated, the solution neutralized and distilled until no iodoform reaction could be obtained with the remainder in the flask. The distillate was then saturated with potassium carbonate, again fractioned, and this process

[1] The sealed tubes are slightly attacked when heated with pure baryta water, but this is scarcely the case with the determinations which were made, as only a slight excess of the reagent was used for saponification so that but little of the base was left to attack the glass. Nevertheless, I made blank determinations so as to ascertain the utmost quantity of insoluble material to be obtained in this way from baryta water and glass, and have deducted this amount from the carbon dioxide found, so as to find the *lowest possible* limit. Taking these experiments into consideration, the above numbers for carbon dioxide would be 30.8 and 32.5 per cent.

continued until the fluid was nearly anhydrous, when it was finally twice distilled from pieces of caustic potash. It then boiled between 60° and 80°. This liquid was now carefully mixed with a concentrated solution of sodium bisulphite, when the whole changed to a semi-solid mass of acetone sodium bisulphite. This was filtered off, the filtrate distilled from sodium carbonate, and the distillate again treated as above until an anhydrous fluid was obtained which was entirely free from acetone. This liquid, when perfectly free from water, boiled at 78° and analyses proved it to be pure *ethyl alcohol*. The quantity of ethyl alcohol was found to be *less than one-half* of the total organic matter obtained by the process of saponification, the greatest care having been taken to prevent any loss during the various processes which have been detailed. The fraction boiling at 128°, therefore, breaks down into carbon dioxide, *ethyl alcohol*, and *acetone*, and the relative proportions of the latter are such that the oil in question must have contained the ethyl-isoacetone ester of carbonic acid.

The same methods of saponification and subsequent isolation of the products of the reaction were repeated with all of the other portions with successively increasing boiling-points; the fraction between 130° and 132° gave practically the same results, while that between 132° and 137° yielded *isopropyl* alcohol in addition to ethyl alcohol and acetone. I also made an attempt to determine, quantitatively, the amount of acetone obtainable from the oil boiling between 132° and 137° (in the other cases I had only decided on the relative proportion of this substance from the difference between the quantity of alcohol and the total anhydrous organic liquid) and found the same to be, at the very least, 30 per cent. of the whole.[1]

If all of the results which have been detailed above are

[1] It is my experience that the amount of acetone which is present in a mixture of that body with ethyl and isopropyl alcohol, is not accurately determinable by any of the methods at present in use. In attempting to separate the acetone by the sodium bisulphite reaction, the loss is so great, owing to the solubility of the compound formed and to its decomposing when exposed to the air, that not even approximate results are obtainable. On the other hand the ammonium iodide, ammonia, and iodine reaction ceases before all of the acetone is converted into iodoform. It is possible that, in the future, I may be able to develop a method which will yield good results. As matters now stand, the above 30 per cent. represents less than the real quantity of acetone.

taken into consideration at the same time, the conclusion becomes inevitable that at least a portion of the acetone must be present in the original oil as carbonic ethyl isoacetone ester, for, even if we assume an extreme case, *i. e.*, that we are here dealing with a mixture of carbonic diethyl ester and some reduction product or ester of mesityl oxide, so that all of the acetone obtainable by saponification might have been derived from the latter, then, with the same percentage of carbon and hydrogen found on analysis, the *proportion of carbon dioxide* would of necessity be much less than that which is really obtainable, for every trace of organic substance which is not present as an ester of carbonic acid, must, evidently, reduce the percentage of dioxide, so that the figures for the latter would fall below 30, when the amount of acetone is above that number. Indeed, the results which have so far been obtained would justify one in assuming that the fraction from 128° to 130° was in reality, the pure body having the formula, $CH_3—COCO_2C_2H_5$, did not some further experiments prove

$$\begin{matrix} & \| \\ & CH_2 \end{matrix}$$

that, contrary to my expectations, it is in all probability a mixture.

Decomposition of the Oil Between 130° and 131° with Phosphorus Pentachloride.

If the oil boiling between 130° and 131° is heated at 120°, for three or four hours, in a sealed tube with somewhat less than the calculated quantity of phosphorus pentachloride, a considerable pressure is produced, even if the container is opened while it is being cooled in a freezing-mixture. The gas which escapes is ethyl chloride. After opening the tube the entire liquid was poured into a fractioning flask and distilled. A considerable quantity of phosgene (boiling-point 8°) first passed over, the thermometer then rapidly rose to 23°, between which temperature and 25° a large proportion of a colorless oil was collected, while the remainder was divided into a part boiling from 95° to 105°, and one above the latter point. All of these fractions were now placed in contact with ice and allowed to stand until the carbonyl chloride and phosphorus oxychloride were decomposed. The second fraction

was afterward dried over calcium chloride and distilled. It now boiled constantly at 23.5° and on analysis gave 45.6 per cent. of chlorine (calculated for $CH_3.CCl:CH_2$ (2-chlor-propene) 46.4 per cent. [B. p. 23.5°]). It is evident, from the above, that this organic halide is derived from the isoacetone of carbonic ethyl-isoacetone ester. The fraction 95° to 105° contained chlorcarbonic ester, so that the following reactions had taken place:

I. $CO(OC_2H_5)(OC_3H_5) + 2PCl_5 = 2POCl_3 + COCl_2 + ClC_2H_5 + ClC_3H_5$.

II. $CO(OC_2H_5)(OC_3H_5) + PCl_5 = POCl_3 + ClCO_2(C_2H_5) + ClC_3H_5$.

The most remarkable part of the reaction is, however, found in the fact that, after removal of the phosphorus oxychloride from the fraction above 105°, the latter proved itself to be a small quantity of pure *carbonic diethyl ether*. The most probable theory is that this body was present in the original oil[1] and that it was there formed by double decomposition between the various esters. It is possible, however, that this double decomposition took place during the continued heating in the presence of phosphorus pentachloride, as follows:

$$2CO(OC_2H_5)(OC_3H_5) = CO(OC_2H_5)_2 + CO(OC_3H_5)_2.$$

In either event, the carbonic diethyl ester, being the most stable organic body present, remains, in part, unchanged. If the first supposition (*i. e.* that the diethyl ester was present in the original oil) is true, then it is necessary to assume (in order to conform with the analytical data which were obtained) that carbonic di-isoacetone ester was also present. In all probability a small quantity of the latter body is formed during each fractionation. And this fact makes it intelligible why traces of low-boiling and high-boiling oils are present after each distillation, even of a product which had previously passed over within 0.5°.

Summary.

The fraction boiling between 130° and 131° is therefore, probably, nearly all carbonic ethyl isoacetone ester, mixed with

[1] It could not have been present in the chlorcarbonic ester used for the reaction, for I used a product which had been most carefully purified.

small quantities of carbonic diethyl and of di-isoacetone ester. The lower portions contain more of the former body (as is proven by the analyses), the higher more of the latter; the part between the 132° and 137° also contains some of the *isopropyl* derivative. The chief result of the entire investigation, and the fact which I have been endeavoring to prove to my satisfaction is that a true carbonic ester of isoacetone is present among the products of the reaction between sodium acetone and chlorcarbonic ester, so that sodium acetone must, of necessity, have the structure represented by the formula, $CH_3.CONa:CH_2$.

The only point which remains unexplained is the high percentage of hydrogen found by means of the analyses. This discrepancy must evidently be due to the presence of a body which is decomposed into acetone, or acetone and ethyl alcohol (possibly isopropyl alcohol), by boiling with hydrochloric acid, and which does not react with phenylhydrazine, (as mesityl oxide would do). Such a body, having the boiling-point of the mixture in question, could be an ethyl ether of mesityl oxide,

$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!C=CH-\underset{\underset{CH_2}{\|}}{COC_2H_5}.$$

This substance would react in the above manner, and its presence would also increase the amount of carbon and of hydrogen. Very much of this ether can, however, not be formed, for its occurrence would materially diminish the amount of carbon dioxide to be found on analyses, although a mixture of carbonic diethyl ester with this ether of mesityl oxide might give carbon and hydrogen percentages which would be the same as those which were found. It must always be borne in mind that more than 30 per cent. of the total organic fluids obtainable by saponification (even in the most unfavorable fraction, 132° to 137°) consists of acetone, while the percentage of the latter body in the lower portions is much higher. Any theory, other than that of the existence of a large proportion of isoacetone-ethyl ester of carbonic acid, is, by the above reasoning, excluded.

The High-Boiling Oil.

The portion of the original oil which boiled above 170° was mixed with pure phenylhydrazine, with the purpose of removing phorone, and other condensation-products of acetone.[1] After standing for some hours, this mixture was distilled in a current of steam and the yellow oil which passed over, washed with dilute hydrochloric acid, dried, and fractioned under diminished pressure; by this means a body boiling at 114° (30 mm.) can be isolated. The analytical results show that the formula to be assigned to this substance is $C_9H_{14}O_3$ while the vapor density (Hofmann's apparatus, vapor of aniline) indicates a molecular weight of 170. This oil has an ethereal odor which suggests that of mesityl oxide, and it is decomposed on boiling with hydrochloric acid into acetone, alcohol, and carbon dioxide.[2] These results agree with the theory that we have here an isomesityl-oxide-ethyl ester of carbonic acid, $(CH_3)_2C=CH-CO-CO_2C_2H_5$, and there is but little

$$\begin{array}{c} \\ \\ \| \\ CH_2 \end{array}$$

question that this body is in reality present. If this theory be correct, however, we must presuppose the existence of a sodium compound of mesityl oxide, and it will be my endeavor, in the future, to isolate this interesting and, presumably, very active substance.

It is interesting to observe that, among all of the products formed by the interaction of sodium acetone with chlorcarbonic ester there is none which indicates that processes of addition take place during the changes which go on. I had expected to find that aceto-acetic ether, or some of its derivatives would be formed in considerable quantity, just as I obtained mono- and dibenzoyl acetone under similar circumstances. The absence of such bodies in the final products does not, however, exclude their temporary formation altogether, for, as I pointed out in the introduction, the presence of sodium carbonate in the solid inorganic precipitate must be due to processes of decomposition. It is not impossible that sodium aceto-acetic ester is produced by the

[1] The latter substances form the larger proportion of the high-boiling oil.

[2] The amount of CO_2 given off was determined. Calculated $CO_2 = 25.8$, found, 24.2. The number is low because a slight remainder was undecomposed.

addition of chlorcarbonic ester to sodium acetone and by the subsequent separation of hydrochloric acid:

1. $CH_3.CONa : CH_3 + ClCO_2C_2H_5 = CH_3.CONaCl.CH_2.CO_2C_2H_5$

2. $CH_3.CONaCl.CH_2.CO_2C_2H_5 = CH_3.CONa : CH.CO_2C_2H_5 + HCl$

for the presence of free pinacone in the original products is abundant evidence of the action of some acid. It does not seem likely, however, that this sodium aceto-acetic ester would be so readily decomposed as to escape detection, although if it were to break down in the presence of alkalies, it would yield sodium carbonate, ethyl alcohol, and acetone. But sodium aceto-acetic ester might react with sodium acetone and the body or bodies so produced may be unstable. This question is obviously one which necessitates future investigation. So long as no processes, such as the above, can be clearly demonstrated, and so long as we can account for the presence of sodium carbonate by other and plausible means, we are not justified in assuming the existence of addition-products.

During the past year I have also endeavored to ascertain whether free acetone possesses the structure of an alcohol, just as its sodium compound has that of an alcoholic derivative, but the decision of this question is fraught with much greater difficulty. According to my experience, acetone reacts neither with acetyl chloride, benzoyl chloride, nor with acetic or benzoic anhydrides in such a manner that the iso-acetone esters of the acid in question are formed, as would be expected were acetone really an alcohol. Processes involving condensation, of course, take place to a certain extent. On the other hand, Kane has shown that a soluble barium compound (presumably of a constitution similar to that of the salts of ethyl-sulphuric acid) is obtainable by treating very cold acetone with sulphuric acid, with subsequent addition of barium carbonate.

Work done in my laboratory indicates that the so-called hydrazone of acetone has a structure represented by the formula

$$\begin{array}{l} CH_3 \\ | \\ C.NH.NH.C_6H_5 \\ || \\ CH_2 \end{array}$$

as the following considerations will show. When the above compound is mixed with considerably less than the calculated quantity of benzoyl chloride, (dissolved in dry toluene), a slow reaction sets in, and after some days a crystalline body separates. This body, insoluble in toluene, is the hydrochloride of the above hydrazo-compound. After this substance had been separated by filtration, it was noticed that the toluene solution had divided into two layers, the lower one of which was a thick oil. The upper layer was removed and carefully distilled in a vacuum. *It contains no acetone.* The lower thick oil was now repeatedly washed with ether, and each ethereal extract tested for acetone. Only traces of the latter substance were found. The ether was now removed from the thick oil, and the latter was then covered with dilute alcohol, containing a little hydrochloric acid, and then the whole gradually changed to a white crystalline solid, while the *alcoholic solution* contained a considerable quantity of acetone, which was isolated in the form of the sodium bisulphite compound. The crystalline solid, on recrystallization from absolute alcohol, melted at 178°, and proved to be dibenzoylphenylhydrazine. No matter how small the quantity of benzoyl chloride in proportion to the phenylhydrazine derivative of acetone (phenylhydrazo -2- propene), the same thick oil is always formed and the latter, with dilute alcohol or with water, always yields dibenzoylphenylhydrazine and acetone. There seems to be no doubt therefore, that the above thick oil is the dibenzoyl derivative of this hydrazo compound, and that, therefore, the phenylhydrazine derivative of acetone contains two hydrogen atoms, attached to nitrogen and replaceable by benzoyl, its structure, therefore, is $\begin{array}{l} CH_3 \\ | \\ C.NH.NH.C_6H_5 \\ || \\ CH_2 \end{array}$. This fact does not, however, in my iopinion prove that free acetones

in reality β-allyl alcohol, for the action of phenylhydrazine on acetone can easily be one of addition, with subsequent separation of water. The phenylhydrazine derivative of acetone is, furthermore, readily oxidized by means of mercuric oxide, when it is in gasoline solution and all air is excluded. The resulting product is a deep red oil which I have not, as yet, been able to crystallize. The phenylhydrazine derivative of benzophenone, which undoubtedly is a hydrazone, is much less readily produced than the corresponding acetone compound and is not readily oxidizable. I intend to give a more complete description of the above work at a future time, when I will also detail the results obtained with the phenylhydrazine derivative of acetophenone and enter into a discussion of the theoretical bearing of the reactions studied. I have also undertaken some work with acetoxime which tends to show that the structure of that body is

$$\begin{matrix} CH_3 \\ | \\ C.NHOH. \\ || \\ CH_2 \end{matrix}$$

This fact is especially brought out by the behavior of benzoylacetoxime. In the meantime, until the above investigations are prepared for complete publication, I beg my colleagues to allow me to reserve this field.

In closing I wish to take the opportunity of thanking Mr. R. R. Putnam for his valuable and energetic assistance in the work which has already been accomplished.

ANN ARBOR, *August*, 1894.

II.—THE ACTION OF METALS ON NITRIC ACID.

2. THE REDUCTION OF NITRIC ACID BY COPPER AND BY LEAD.

BY GEORGE O. HIGLEY.

A short time ago[1] I published (in conjunction with P. C. Freer) a preliminary notice on the action of copper on nitric acid, giving a few results of work done with an acid of the

[1] This Journal, **15**, 71.

specific gravity 1.40. It was there shown that when the above strength of acid is used, the reduction-product is approximately pure nitrogen dioxide, and my work was confirmed by that of Montemartini,[1] who began his investigations in this field at about the same time. As my research was inaugurated before the article of that investigator appeared, and as, in several respects, it is conducted according to quite different methods, and as, moreover, his results, as a rule, account for more than 100 per cent. of the metal dissolved,[2] thus necessitating the theory that water takes part in the reactions between the metals and nitric acid, I have decided to continue my own research with the purpose of definitely settling the relation to be found between the nature and proportions of the reduction-products and the strength of acid used.

Early in the progress of this work several improvements were made in the apparatus described in the previous paper. The generating flask was changed as follows: Within the neck of an ordinary fractionating flask, of about 250 cc. capacity, was sealed a glass tube with an internal diameter of about five mm. and reaching nearly to the bottom of the flask; the upper end of this tube was connected, by means of a ground-glass joint, with the tube containing the acid. The stirring rod was discarded, it being thought that the liquid would be sufficiently agitated by the current of carbon dioxide constantly passing through it during solution of the metal. The joints, which were described as sealed with high-melting paraffin, were entirely replaced by those of ground glass. The nitrous and nitric oxides were collected in a gas tube over a 50-per cent. potash solution (previously saturated with nitrous oxide), and, after the removal of nitric oxide by means of an excess of oxygen, the residual gases were transferred to an explosion eudiometer over mercury, and their composition determined according to the usual methods.

The copper employed was chemically pure, and in the form of foil one-tenth mm. in thickness. The volume of acid taken was always increased with diminishing specific gravity, so that in no experiment was the quantity present less than ten times the amount requisite for the solution of the metal. Experiments

[1] Gazetta Chimica Ital., **22**, 397. [2] *Ibid*, **23**, I., 250 and 277.

were usually undertaken in duplicate, and in each determination with an acid having a specific gravity of 1.25 or greater, two titrations of nitrosyl-sulphuric acid, and two nitrometer analyses were made.

Method of Stating Results.

In order to facilitate the comparison of results obtained under varying conditions, tables are given showing: 1. Temperature during solution. 2. Volume and specific gravity of acid. 3. Weight of nitrogen trioxide obtained from titration of nitrosyl-sulphuric acid contained in the Winkler tube. 4. Weight of trioxide from nitrometer analyses. 5. Weights[1] of trioxide and dioxide absorbed by the sulphuric acid with equivalent weights of metal. 6. Volumes of nitric and nitrous oxides, with respective metal equivalents. 7. Total metal dissolved and per cent. equivalent of metal found. These results are also finally given in the form of curves (p. 26.), with the specific gravity of the acid as abscissae and the per cent. of metal equivalent, as ordinates.

The results of work done with copper are to be found in Table I. It will be observed that nitrogen is not given among the products of the reduction by copper of nitric acid of any degree of concentration. The small and fairly constant quantities of nitrogen found in the eudiometer after each explosion, were probably due to traces of air present in the carbon dioxide with which the oxides of nitrogen were swept forward, since blank tests maintained for two hours (the average time of a determination) resulted in the collection of appreciable quantities of air.

No nitrous oxide was obtained with acid solutions having a specific gravity greater than 1.15; the amount then increases with acid of specific gravity 1.10, and afterwards, contrary to expectation, it slightly decreases.

Nitric oxide was not found among the gases obtained by reduction of an acid of a specific gravity above 1.25; with greater dilution there is an increase of this gas, the course of which can best be followed from the corresponding curve in the appended diagram.

[1] For the method of calculation, see This Journal, 15, 78.

Nitrogen dioxide and trioxide in varying proportions are the sole products of reduction of nitric acid of specific gravity of 1.30 to 1.40.

While the amounts of trioxide, as determined by means of permanganate solution, are substantially constant, amounting to from 96.5 to 100 per cent. of the copper dissolved, the amount of trioxide from the nitrometer analyses shows a decided diminution with each successive dilution of acid, dropping from 315.7 milligrams (or nearly double the quantity obtained from the permanganate determination) to 68.5 milligrams, (an amount practically in agreement with the latter[1]).

Apparently then, copper reduces strong nitric acid to nitrogen dioxide, and the latter, when it is expelled from the resulting solution by heat, passes over with but little decomposition to be absorbed by the sulphuric acid with the formation of nitrosyl-sulphuric and nitric acids. When such a solution of nitrogen dioxide is titrated by means of permanganate, there will be found one-half as great a quantity of trioxide as will be shown by the nitrometer.

In the reaction between nitric acid (specific gravity 1.35) and copper, the dioxide which is at first formed, undergoes further decomposition because the water which is present produces nitric acid and nitric oxide, the latter afterwards reacting with nitrogen dioxide so as to generate the trioxide. When copper is dissolved in nitric acid of still greater dilution, the decomposition of dioxide is increased to such an extent that when the specific gravity of 1.25 is reached it has entirely disappeared as such, as is proven by the practical equality of trioxide obtained in the permanganate and nitrometer analyses of the sulphuric acid (expt. 8); while, at the same time, 39 cc. of nitric oxide can be collected at this stage of the dilution.

With acids whose specific gravity diminishes below 1.25, the weight of trioxide steadily decreases, while the volume of nitric oxide advances.

[1] The relation between the nitrogen dioxide and trioxide is shown by the relation between the permanganate titration and the nitrometer results. For the method of calculation, see *loc. cit.*, p 78.

I. Action of Copper on Nitric Acid.

Experiment No.	Temperature.	Acid. Volume.	Acid. Sp. Gr.	Winkler tube. Mgs. N_2O_3.	Nitrometer. Mgs. N_2O_3.	Nitrogen dioxide. Mgs.	Equivalent metal. Mgs.	Nitrogen trioxide. Mgs.	Equivalent metal. Mgs.	Nitric oxide. cc.	Equivalent metal. Mgs.	Nitrous oxide. cc.	Equivalent metal. Mgs.	Metal found. Mgs.	Metal dissolved. Mgs.	Per cent. metal found.
1	65	65	1.05	6.45	.....	0	0	6.45	10.73	58.5	248.73	2.61	29.54	289.09	300	96.36
2	60	65	1.05	6.31	.....	0	0	6.31	10.5	59.6	253.0	2.31	26.14	289.6	"	96.54
3	65	60	1.10	16.02	.....	0	0	16.02	26.6	54.6	231.5	3.36	38.03	295.5	"	98.5
4	25	60	1.10	24.1	.....	0	0	24.1	33.3	52.36	222.1	4.05	45.8	300.5	"	100.5
5	20	50	1.15	34.15	.....	0	0	34.15	56.7	51.57	218.6	1.35	15.27	290.7	"	96.9
6	20	40	1.20	40.4	.....	0	0	40.4	67.2	52.2	221.6	Lost.	....	286.8	"	95.5
7-8	20	40	1.15	60.49	.....	0	0	60.49	100.7	45.9	194.9	....	....	295.6	"	98.5
9	20	30	1.25	74.16	.....	0	0	74.16	123.6	39.0	165.6	....	....	289.0	"	96.3
10	20	15	1.30	173.27	68.5	76.7	54.74	141.4	235.59	....	.....	....	....	294.3	"	98.1
11	17	10	1.30	170.64	204.9	177.4	144.2	150.3	250.2	....	....	....	....	294.4	"	98.14
12	17	10	1.35	170.0	281.5	177.9	122.43	104.03	173.2	....	....	....	....	295.63	"	98.54
13	0	9	1.40	180.2	320.4	340.5	234.18	49.0	156.7	....	....	....	....	296.1	"	98.7
14	15	9	1.40	178.63	314.9	339.9	226.9	42.3	70.4	....	....	....	....	300.77	"	100.25
15	50	9	1.40	180.2	315.7	327.9	225.5	44.7	74.41	....	....	....	....	297.3	"	99.09
														299.9	"	99.9

II.—*Reduction of Nitric Acid by Lead.*

The results as given in Table II, were obtained from work with acids of specific gravity 1.05 to 1.35. Experiments made with stronger acids were not successful, since the insolubility of lead nitrate in strong nitric acid prevented the solution of the metal, because of the protective coating of salt formed about the latter. It will be observed that, while the reduction-products are the same as in the parallel work with copper, there is a striking difference in the relative amounts of the oxides of nitrogen produced. Thus, while the nitrous oxide equivalent of copper with 1.10 per cent. acid is only 13–15 per cent. of the metal, with lead it is as high as 62 per cent. The difference in the results obtained with the more dilute acids is even greater, and reference to the curves will show that the same contrast in the reducing power of lead and copper is found throughout the whole work. As experiments have not been made to determine the effect of temperature upon the composition of the products of reduction of *dilute* nitric acid by copper, it cannot be asserted that *all* of the observed differences in the results of the reactions with copper and lead are due to differences in the strength of metallic properties. Judging, however, from the results of experiments 1, 2, and 3, Table I, it is probable that the effect of varying temperature, for any degree of concentration of the acid, is but slight. That lead is a much more pronounced metal than copper, and that, therefore, the observed differences are to be expected, is clear from the thermo chemical investigations of Thomsen.[1] That investigation gives the number of heat units evolved in the formation of nitrates in aqueous solution [according to the formula (R,O,QAq)] for copper and lead respectively, as 52,910 and 68,070, and also the number of units evolved in the action of gaseous hydrogen acids on water-free oxides, as follows:

CuO, and PbO+2HCl; 38,830 and 56,830;

CuO, and PbO+2HBr; 46,900 and 65,630;

CuO, and PbO+H_2S; 33,750 and 49,830,

[1] Thermochemische Untersuchungen, III., 514 and 518.

II. Action of Lead on Nitric Acid.

Experiment No.	Temperature.	Acid. Volume.	Acid. Sp. gr.	Winkler tube. Mgs. N_2O_5.	Nitrometer. Mgs. N_2O_5.	Nitrogen dioxide. Mgs.	Equivalent metal. Mgs.	Nitrogen trioxide. Mgs.	Equivalent metal. Mgs.	Nitric oxide. cc.	Equivalent metal. Mgs.	Nitrous oxide. cc.	Equivalent metal. Mgs.	Total metal found. Mgs.	Metal dissolved. Mgs.	Per cent. found.
1	0°	65	1.05	17.07	....	0	0	17.07	93.75	13.99	180.16	19.04	704.2	977.16	1000	97.71
2	"	65	1.05	10.99	....	0	0	10.99	59.85	15.49	214.88	18.9	699.66	973.75	"	97.37
3	"	60	1.10	29.96	....	0	0	29.96	162.5	11.6	161.1	16.8	621.4	945.07	"	94.50
4	"	55	1.15	18.97	....	0	0	18.97	102.77	30.3	420.3	13.01	481.2	1004.3	"	100.4
5	"	50	1.20	20.4	....	0	0	20.4	110.93	31.6	438.3	10.9	403.17	952.4	"	95.24
6	"	40	1.25	24.28	....	0	0	24.28	134.14	39.94	553.51	8.15	301.43	987.08	"	98.70
7	"	20	1.30	27.69	28.49	0	0	27.69	150.62	43.88	633.77	4.39	162.36	946.7	"	94.67
8	"	25	1.35	70.17	103.68	55.43	124.5	57.26	311.6	24.4	338.5	4.51	166.5	941.1	"	94.11

In regard to the immediate source of nitrous oxide in reactions such as those we are considering, several explanations have been offered. Divers[1] has shown that hyponitrous acid decomposes readily into nitrous oxide and water and V. Meyer[2] has proven that hydroxylamine and nitrous acid react in a similar manner. Divers has also demonstrated[3] that in the preparation of hydroxylamine by the action of tin on nitric acid, a much better yield is obtained if a second acid (such as sulphuric or hydrochloric) is present. I am not aware, however, that any work has been done to determine the respective quantities of nitrous oxide obtained from the solution of equal weights of metal in nitric, and in a mixture of nitric and sulphuric acids. Accordingly, near the close of the present work, I made a determination with one gram of lead, employing as a solvent, 65 cc. of nitric acid (specific gravity 1.05), and 2 cc. of concentrated sulphuric acid. The action, of course, was greatly retarded by the coating of lead sulphate on the surface of the foil so that at the close of four hours only 888 milligrams of metal, had dissolved ; yet an analysis of the gases and a calculation to one gram of lead showed a yield of only 12.27 cc. of nitrous oxide, which represented a deficiency as compared with the parallel experiments (Table II, 1 and 2) of about 33 per cent. However, as the volume of nitric oxide collected was also low, no definite conclusion can be drawn from this fact. It is my intention to repeat these experiments while examining the resulting solution for hydroxylamine sulphate, with a view of determining definitely whether the source of nitrous oxide in this reaction is not to be found in the decomposition of hydroxylamine.

Conclusions.

1. Nitric acid of specific gravity of 1.30 or greater, when reduced by copper, yields only nitrogen trioxide and dioxide, the former increasing and the latter diminishing rapidly with increasing dilution of the acid.

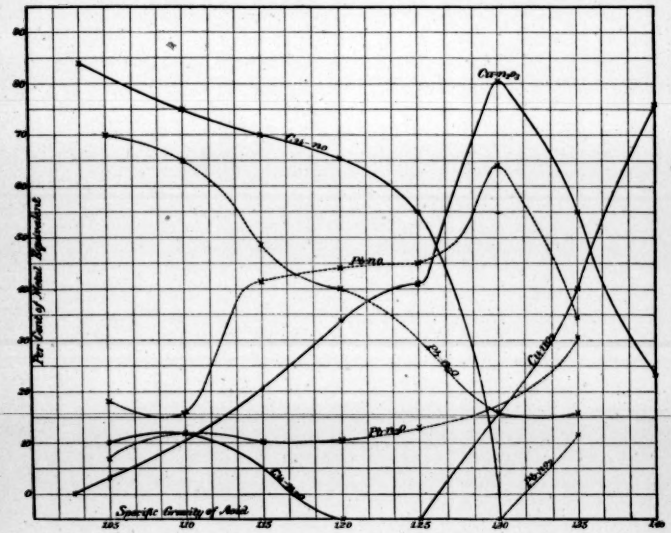
2. Nitric oxide is a product of decomposition of nitrogen trioxide and dioxide, when the specific gravity of the nitric

[1] Proc. Lond. Roy. Soc., **19**, 425. [2] Ann. Chem. (Liebig), **175**, 141.
[3] J. Chem. Soc., **43**, 455.

acid employed is 1.25 or more; if the acid has a specific gravity below 1.25, then the trioxide only is the source of nitric oxide.

3. Lead reacts much more readily than copper, producing, with equal concentration of acid, relatively much more nitrous oxide and less of the higher oxides of nitrogen.

4. While not desiring to generalize on a too slender basis of experimental evidence, it seems to me that the remarkable difference in the compositon of the products of reduction of nitric acid by lead and copper, respectively, favors the direct deoxidation theory, rather than the one which presupposes the presence of nascent hydrogen.



ANN ARBOR, *July*, 1894.

III. AN INTRODUCTORY STUDY OF THE INFLUENCE OF THE SUBSTITUTION OF HALOGENS IN ACIDS, UPON THE RATE AND LIMIT OF ESTERIFICATION.

By D. M. Lichty.

The classic work on esterification, by Berthelot and Péan de Saint-Gille,[1] and particularly the study by Menschutkin,[2] of the influence of the isomerism of alcohols on the rapidity and limit of esterification, suggested the use of the same process for determining the influence which substitution of halogens in fatty acids has upon the rate and the limit of their esterification. The study was begun with ordinary alcohol and monochloracetic acid. No material was used whose purity was not first assured. The investigation was carried out by heating one or more series of mixtures of equivalent weights of alcohol and an acid. These mixtures were sealed in small tubes. The quantity of alcohol used for each trial was as nearly 0.250 gram as could be readily weighed; the capacity of the tubes was about 7.5 cc., and all were as nearly of the same size as they could be conveniently made.[3] To prevent any esterification before heating, the following method was employed:

The alcohol was enclosed in sealed, thin-walled bulbs, small enough to be placed into the tubes to be used, then the theoretical quantity of acid was added, and the whole sealed. Immediately before placing into the thermostat any of these small vessels (a series of six or eight of which were heated at one time), the bulbs were broken by a quick shake. The thermostat consisted of an oil-bath, which was kept at a temperature of 154° C. by means of a Lothar-Meyer furnace[4] and a Reichardt gas-regulator. To stop the process of esterification, or at least to reduce it to a minimum after a tube was taken from the bath, it was at once plunged, at first into tepid and then into cold water.

[1] Ann. Chim. Phys., [3], 1862, **63**, 385; **66**, 5; 1863, **68**, 225.
[2] Ann. Chim. Phys., [5], 1880, **20**, 287.
[3] Berthelot and Péan de Saint-Gille: Ann. Chim. Phys., [3], **66**, p. 53 et seq.
[4] Ber. d. chem. Ges., **16**, 1090, Fig. 4.

It was first deemed necessary to discover whether any of the acids, in question, acted upon glass; but neither monochloracetic nor dichloracetic acid had any appreciable effect. No trials were made with the other acids.

For the purpose of determining the amount of acid left uncombined at the end of a trial, I intended to use a standardized solution of barium hydroxide, following Berthelot and Menschutkin; but the first trial proved that the monochloracetic ester is rapidly saponified by this reagent,[1] and further investigation showed that the esters of the other acids are affected in the same way, and, as would be expected, sodium, potassium, and calcium hydroxides produce the same result. Experiment developed the fact, however, that ammonia does not readily saponify, for it was shown that the weight of an acid found by titrating by means of this reagent, using a mixture of an acid and its ethyl ester, differed only by a few tenths of a milligram from the weight actually taken. Magnesia was also used to determine the amount of free acid in two series of esterifications of monochloracetic acid. The results of these trials are given in the following tables:

Duration of esterification.	1 hour.	2 hours.	4 hours.	6 hours.	
Series I.	67.98	72.04	65.70	69.34	per cent. esterified.
Series II.	67.46	71.02	69.74	65.21	" "

Duration of esterification.	8 hours.	10 hours.	12 hours.	54 hours.	
Series I.	68.61	67.31	....	34.78	per cent. esterified.
Series II.	65.82	67.79	67.09	46.93	" "

The figures beneath the number of hours during which a tube and its contents had been heated, represent the per cent. of the acid which was esterified, *i. e.*, at the end of the first hour in Series I, 67.98 per cent. of the monochloracetic acid was esterified, while at the end of the same interval in Series II, 67.46 per cent. of the acid was esterified, and so on.

The results with ammonia as the titrating reagent were as follows:

Duration of esterification.	1 hour.	2 hours.	4 hours.	6 hours.	8 hours.	54 hours.
Per cent. esterified.	67.01	66.78	66.91	66.61	65.81	45.58

[1] The use of barium hydroxide as a means of determining the amount of unchanged acid, has possibly led to some error in the work of Berthelot and Menschutkin, although it is probable that the esters of non-substituted acids are much less rapidly saponified than are those under consideration.

The ammonia method for determining the free acid was finally definitely adopted for it was found to be much less liable to error than the one in which magnesia was used, the latter yielding no concordant results with known weights of acid while the former did. As it was discovered that water very slowly saponifies the esters, the contents of each tube after the heating, were dissolved in alcohol before titrating for free acid. The results obtained with magnesia are given mainly to show that the low per cent. of esterification attained at the end of 54 hours was not due to experimental error. No gaseous products were formed and no explanation for the low figures can now be offered, although they are undoubtedly due to some decomposition.

The per cent. of acid esterified at the end of the first hour or the "initial rate of esterification" is 67.01, while this is also the highest per cent. reached, and, therefore, the limit. The average of the first five trials is 66.62, the mean limit of esterification. The initial rate for acetic acid and ordinary alcohol is 46.95,[1] while the limit, which is reached in about 24 hours, is 66.57.

Esterification of Dichloracetic Acid.

Duration.	1 hour.	2 hours.	4 hours.	6 hours.	8 hours.	10 hours.
Series I.	69.32	69.98	69.42	70.93	69.99	71.39
Series II.	71.00	71.26	71.20	70.97	70.83	70.44

Here again the initial rate and the limit are practically the same, the average of all the results being 70.65, that of the first series 70.24, and of the second 70.95. The average initial rate is 70.16.

Esterification of Trichloracetic Acid.

No satisfactory results were obtained with this acid, because secondary changes, causing the evolution of gas, took place. Owing to the explosion of the tubes while being heated, only one determination of free acid was secured, the result showing that about 6.5 per cent. of the acid remained uncombined, or that 93–94 per cent. of the acid was neutralized. The presence of gas as a product of the reaction, makes it extremely doubtful whether these figures indicate the true amount of

[1] Menschutkin: Ber. d. chem. Ges., 11, 1507 b; Ann. Chim. Phys., [5], 20, p. 305.

acid which was esterified, as the hydrochloric acid evolved would assist in the dehydration.

Comparison of Results.

	Initial rate.	Limit.
Acetic acid	46.95	66.57
Monochloracetic acid	67.01	66.62 (average of 5)
Dichloracetic acid	70.16	70.65 (average of 12)

The limit for acetic acid is reached in about 24 hours, while that for the mono- and the dichloracetic is reached, as will be seen below, even in half an hour. The initial rate increases with the increase in the amount of chlorine. The limits for acetic acid and monochloracetic are nearly equal, while that for dichloracetic acid is about four units higher. It will also be seen that the difference between the initial rates for acetic acid and that for monochloracetic is about 20 units, and, between the initial rate for monochloracetic acid and that for dichloracetic, three units. The influence of chlorine is then by no means proportional to the number of atoms of that element, which are contained in the molecule.

In the three 54-hour determinations with monochloracetic acid, which gave lower results than those which were obtained at the end of one hour, no gaseous products were detected. No explanation can be offered for the results obtained until a more careful examination of the products be made.

One trial with each of the two chloracetic acids in which the reaction continued for a half-hour only gave the following results:

Monochloracetic acid	68.04
Dichloracetic acid	71.14

These results are higher than are those of the average limit already given.

Esterification of Monobromacetic Acid.

Duration.	½ hour.	1 hour.	4 hours.	8 hours.
Series I.	65.87	62.67	50.82	43.46

This series shows a rapid decrease in the per cent. of acid esterified with increase in the duration, a decrease which begins to show itself after a shorter period than in the case of monochloracetic acid and is much more marked than for the

latter acid. No gaseous products were noticed in this connection. The amount of acid esterified at the end of one-half hour is a little over two units less than in the case of monochloracetic acid.

It is very evident that the rate of esterification is remarkably accelerated by the substitution of halogens for hydrogen in acetic acid, and that in the case of the two monohalogen acids studied, a secondary reaction sets in early and causes an increase in the quantity of free acid.

I hope to conduct this investigation under more favorable conditions as to temperature, if possible, and to make the intervals, especially at the beginning, much shorter so as to make it possible to follow the course of the reactions more completely. The research will also be extended to other series of halogen substituted acids, besides those from acetic acid, with the hope of obtaining a large number of data from which to determine the influence of the position as well as of the number of substituting halogen atoms upon the rate of esterification. The especial and new problem to be attacked is, however, to ascertain the *true* initial velocity in these cases, by selecting lower temperatures than those adopted by previous investigators, and by also beginning the determination at the *shortest possible* interval after immersing the mixture of acid and alcohol in the thermostat.

ANN ARBOR, *June*, 1894.

IV. ON THE ACTION OF SODIUM ON THE ESTERS OF ACONITIC AND CITRIC ACIDS. PRELIMINARY NOTICE.

BY PAUL C. FREER.

If perfectly pure triethyl aconitate is dissolved in ten times its own volume of ether and the calculated quantity (one molecule) of sodium, in the form of finest wire, is then added, reaction sets in at once; the sodium becomes covered with a yellow solid, while hydrogen is evolved, the ether at the same time assuming a deep red color. If the sodium is kept clean by means of a stirrer, it gradually disappears, while the above-mentioned precipitate takes its place. A substance, having

the same composition, is also produced if sodium ethylate, in calculated quantity, is added to an ethereal solution of triethyl aconitate. In the latter reaction a deep red color is at first observed. After a few minutes the liquid becomes turbid, and finally a yellow-colored precipitate is deposited which, however,—differing from the one produced by the direct action of sodium,—is deliquescent. This sodium derivative has not the simple formula which would result from the replacing of one hydrogen atom in a molecule of the ester by means of the metal, for analysis shows that it contains 16.2 per cent. of sodium[1] (calculated for $C_{12}H_{23}O_{11}Na_4 = 16.48$ per cent.; or for the sodium derivative of two molecules of triethyl aconitate less one of ethyl alcohol). If either of these sodium derivatives is acidified with dilute sulphuric acid, and the resulting brown solution is extracted repeatedly with ether, a thick oil is deposited upon evaporation of the solvent. The following means of purification were adopted: The oil was dissolved in dilute ammonia, a little insoluble residue filtered out, and the filtrate thereupon precipitated with lead acetate; after the excess of ammonia had been expelled, the resulting lead compound, which was nearly white, was decomposed by means of hydrogen sulphide and then filtered, while the filtrate was repeatedly extracted with pure ether. When the latter was distilled off, a clear, slightly yellow syrup remained, which did not crystallize, even after standing for some days. This syrup reacts readily with phenylhydrazine, forming a non-crystallizable compound; it imparts a deep red color to a solution of ferric chloride, and is undoubtedly a ketone. It is readily saponified by means of alcoholic potash, and a crystalline body, melting at 114°–115° with the formula $C_9H_{12}O_6$ can be isolated after acidifying. The sodium acting on triethyl aconitate, therefore, at first replaces a portion of the hydrogen, while, subsequently, sodium ethylate separates, so that the resulting compound is a ketone.

A similar result is observed when sodium (two atoms) is added to triethyl citrate (one molecule). The hydrogen contained in the hydroxyl group is at first vigorously attacked, but subsequently the excess of metal reacts with the sodium

[1] A second sodium derivative which is soluble in ether, is also produced.

derivative so formed, separating sodium ethylate, and producing the metallic derivative of a ketone, which contains 16.5 per cent. of sodium, and is, in appearance, like that obtained from triethyl aconitate. The above experiments have also been extended to tetraethyl citrate, triethyl aconitate, and to triethyl carballylate with similar results.

Recently Dieckmann[1] inaugurated some experiments on the action of sodium on tiglic and pimelic acids, obtaining in the first case, by separation of sodium ethylate, a derivative of ketopentamethylene, and, in the second, a similar one of hexamethylene. As the work which I had begun with the ethereal salts of tribasic acids seemed to enter upon the territory taken by Dieckmann with the dibasic ones, I temporarily gave up the work. Personal information recently received by me from Dr. Dieckmann, has left this entire field to me, so that I intend once more to take up the work where I left it.

Miss N. E. Goldthwaite has executed the experimental work which has so far been done in this investigation, and I wish to take this opportunity of most heartily thanking her for her assistance.

October, 1894.

THE COMBINATION OF SULPHUR WITH IODINE.

By C. E. Linebarger.

I.

INTRODUCTION.

Historical.—In the first paper ever published on the properties and reactions of iodine, it is stated that the elements, sulphur and iodine, enter into combination,[2] nothing being said, however, of the nature and properties of the compound.

Gay-Lussac, in his classical monograph on iodine[3] writes that iodine forms with sulphur only a weak combination, which is blackish gray and indistinctly crystalline; no defi-

[1] Ber. d. chem. Ges., **27**, 102, 965.

[2] "Le soufre s' unit à l'iode, mais avec moins d'energie que le phosphore."—B. Courtois: Découverte d'une substance nouvelle dans le Vareck. (Cette découverte a été annoncé le 6 decembre, à la séance de la première classe de l'Institut par M. Clément). Annales de Chimie et de Physique, **88**, p. 308, 1813.

[3] Recherches sur l'iode: Annales de Chimie et de Physique, **91**, p. 22, 1814.

nite compound of the two metalloids, however, is described; indeed, Gay-Lussac regarded the two elements as being so similar in their properties and behavior, that some doubt might be placed in the possibility of their entering into true chemical combination.

Soon after the discovery of iodine, physicians and pharmacists began to look into the medicinal properties of the element and its compounds. Henry, in the *séance* of the 15th of May, 1827, of the *Société de Pharmacie*[1] communicated a process of preparing an "iodide of sulphur," for medicinal purposes, by melting the two elements together in certain proportions; these proportions, it may be stated, were afterwards changed.

Heinrich Rose[2] subjected to sublimation an "iodide of sulphur" made by melting iodine and sulphur together—in what proportions, he does not state. Two experiments were performed, in one of which 88.76 per cent. of iodine was found in the sublimate, while in the other, the per cent. of iodine was 92.56. Rose concludes that no definite compound of the two elements is formed in this way.

For nearly thirty years no further work on this subject seems to have been done. At the beginning of the "sixties," however, several papers appeared almost simultaneously by Rath,[3] Lamers,[4] and Guthrie.[5]

Rath's work consists in a crystallographic examination of some samples of a "hexaiodide of sulphur" prepared by Lamers in the following way: Solutions of sulphur and iodine of various proportions in carbon bisulphide were allowed to evaporate slowly at low temperatures, whereby crystals, containing six atoms of iodine to one atom of sulphur, invariably separated out, no matter what the relative proportions of the two elements in the solution had been, unless indeed, one of

[1] Journal de Chimie Medicale, de Pharmacie et de Toxicologie, redigé par les Membres de la Société de Chimie Medicale, **3**, 313, 1827.

[2] Ueber die Verbindungen des Schwefels mit dem Chlor, Brom, und Jod: Poggendorff's Annalen, **27**, 115, 1833.

[3] Krystallographische Beiträge, 10; Dreifach Jodschwefel, SI_3. Poggendorff's Annalen, **110**, 117, 1860.

[4] Notiz über Jodschwefel; Journal für praktische Chemie, **84**, 349, 1861.

[5] On the Bisulphide of Iodine; Quarterly Journal of the Chemical Society, **14**, 57, 1862.

the metalloids was present in considerable excess, when, before the crystallization of the hexaiodide, the element in excess separated out to some extent first. Rath was inclined to call the crystals examined by him, mere isomorphous mixtures, but hesitated to draw such a conclusion, inasmuch as he regarded sulphur and iodine to be too dissimilar elements to form isomorphous mixtures.

Lamers states that he repeated Grosourdi's experiment,[1] which consisted in passing a current of hydrogen sulphide into an aqueous solution of trichloride of iodine, and thus obtained a reddish-brown amorphous mass having a composition corresponding approximately to the formula S_3I_2.

In Wurtz's Dictionaire de Chimie, under the head of Iodides of Sulphur, it is stated that E. Henry[2] has described the product of the reaction of one atom of sulphur on two of iodine, which possesses a lamellar structure and a feeble odor of iodine.

Guthrie (*loc. cit.*) investigated the reaction between sulphur chloride and the iodides of some alcoholic radicals, the product being an "iodide of sulphur in the form of fine tabular crystals of the luster of iodine." An analysis of the compound showed the simplest assignable formula to be SI.

About a year later, Sestini[3] took up the investigation of melting-points and composition of mixtures of iodine and sulphur, in order to see if there really exists a compound of the two elements in definite proportions. He came to the conclusion that the two elements actually enter into combination forming a number of definite compounds instead of a mere mixture; these compounds are, he writes, in every respect analogous to metallic alloys.

Schlagdenhauffen's[4] paper on the "Iodides of Sulphur" is an important contribution to our knowledge of the subject, although it seems never to have been duly quoted. The

[1] In the dictionaries and text-books of chemistry, the reference to Grosourdi's paper is Jour. de Chim. Medicale, **9**, 429. I have hunted in vain in that journal for the paper, and think that some error, clerical or otherwise, has been committed.

[2] Jour. de Pharm., **13**, 403.

[3] Sur la combinaison chimique du soufre et de l'iode: Repertoire de Chimie appliquée, **5**, 481, 1863.

[4] Sur l'Iodure de Soufre: L'Union Pharmaceutique, **104**, 1874.

writer first determined the points of fusion of a number of mixtures of sulphur and iodine, although not with very great accuracy. He also carried out some experiments on the sublimation of previously fused mixtures of the two elements, with results similar to those obtained by Rose (*loc. cit*). On repeating Lamers' experiments (*loc. cit.*) he found it possible to prepare a large number of compounds having the same crystallographic structure and very similar properties to Lamers' "hexaiodide of sulphur." His words in this connection are worth repeating: "When solutions of iodine and of sulphur in carbon bisulphide are mixed, a colored solution is obtained no matter what the relative quantities of the two metalloids be; no heat is evolved, hence no reaction, no combination; it is nothing but a simple mixture of the metalloids." The experiments of Guthrie were corroborated and similar ones performed. The conclusions arrived at by him are: There exists a great number of compounds of sulphur and iodine, obtainable through fusion and solution, all being of the character of alloys.

The heat of combination and of solution in carbon bisulphide, of a compound of sulphur and iodine, which is stated to have the formula S_2I_2 and "the characters of a definite body," has been determined by Ogier,[1] who found the first to be quite too small to be taken into account, and the second equal to the sum of the heats of solution of the two elements alone in carbon bisulphide.

In order to render complete the historical account of the combination of sulphur with iodine, it is necessary to mention the papers of Hautefeuille[2] and of Menke,[3] in which certain reactions are treated of, which were supposed to yield compounds of the two metalloids, although these were not isolated and examined.

If we consider the papers which have just received brief mention, we feel that the evidence for or against the existence of compounds of iodine and sulphur, according to definite

[1] Sur les chlorures, bromures et iodures de soufre: Comptes rend., **92**, 922, 1881.

[2] Action de l'acide iodhydrique sur quelques chlorures et sulfures: Bulletin de la Société Chimique, (2), **7**, 198, 1867.

[3] Reactions of Iodine and of Potassium Iodide with Sulphurous Acid: Chemical News, **39**, 19, 1879.

Vol. 17
1895

proportions, is of an unsatisfactory nature. That iodine combines chemically with sulphur, seems probable, inasmuch as it is claimed that heat is evolved when the two elements are melted together. Still the act of solution is sometimes accompanied by the liberation of heat, and we may have to do only with a case of solution. It results from the investigations by Schlagdenhauffen (*loc. cit.*) that the two metalloids do not always crystallize out of solution in the proportions given by Lamers (*loc. cit.*). Furthermore, the reaction studied by Guthrie (*loc. cit.*) does not prove that an iodide of sulphur is actually formed, since it is quite possible that the sulphur and iodine are merely set free and crystallize as isomorphous mixtures rather than definite chemical compounds.

Object and Division of Paper.—In order to clear up, as well as possible, the doubts and obscurity about the subject of the combining of iodine and sulphur, I have taken up its investigation, repeating the old, and carrying out new experiments. Within recent years new theoretical and experimental means of deciding such questions have been introduced into science, by the judicious use of which a fair measure of success seems assured.

The division of the paper is as follows. In three sections I shall treat of the combination of the two elements: In the first, by fusion, in the second, in solution, and in the third, by double decomposition. Each of the sections is preceded by a somewhat detailed historical account of work already done, all necessary data being reproduced. This is followed either by a sketch of a theory which throws some light upon the subject, or by experimental work of my own. Then comes naturally the discussion of the results and the conclusions to be drawn from them. In the last section is given a brief *résumé* of the conclusions arrived at.

II.

COMBINATION BY FUSION OF ELEMENTS.

Historical.—Courtois (*loc. cit.*), Gay-Lussac (*loc. cit.*), and others obtained by melting together sulphur and iodine in certain proportions, a brilliant dark gray mass of crystalline structure, fusible at about 60°., insoluble in water, by which

it is decomposed as well as by distillation. Henry (*loc cit.*), who was, I believe, the first to introduce into medicine a fused mixture of the two elements as a definite compound, recommended the taking of eight parts of iodine to one part of sulphur. Later, however, pharmacists prepared the medicament with half the above proportion of iodine. In the Pharmacopie Raisonnée (ou Traité de Pharmacie pratique et théorique: N. E. Henry and G. Guibourt, 3rd edition, 1841) it is stated by the authors that "they prepared it formerly with double the amount of iodine, which, being in excess, was easily liberated through heat, and was lost continually by evaporation; the proportions now adopted constitutes a chemical species more stable in its composition, but which still gives out all the time a strong odor of iodine." This pharmaceutical preparation was incorporated in the French Codex, and afterwards in all pharmacopœias, wherein may be found a full description of its mode of preparation and properties.

Sestini (*loc. cit.*) in seeking an answer to the question as to whether the pharmaceutical preparation is really a true chemical combination of sulphur and iodine, conducted a couple of series of experiments with mixtures of the two elements. In the first series he heated a mixture of known composition on a water-bath. Just as soon as the mass commenced to melt, the temperature was read off on a thermometer inserted in the mass itself, and the whole was agitated while the temperature rose slowly. Then, after it had been left in repose for several minutes, the liquid portion was poured off from the solid portion, and each was analyzed. Four such experiments were performed, the melting-points being 65.5° to 66° for the four mixtures made up of two parts of sulphur to eight parts of iodine, that is, one atom of each element. The solid portion contained from 27 to 31 per cent. of sulphur, and the liquid portion from 10 to 11 per cent. of the same element. In the second series of experiments the mixture of iodine was completely, or almost completely, melted, and then allowed to cool very slowly. The composition was then determined of a mass of crystalline structure found in the upper part of the tube in which the melting had taken place, and of another mass of lamellar structure found in the lower part of the tube.

From the results obtained, Sestini believed he could conclude that chemical combination took place, the compounds formed having a composition varying with the composition of the mixture from which they were deposited.

Schlagdenhauffen (*loc. cit.*) determined the melting-point of eleven mixtures of iodine and sulphur of varying concentrations, but his data are not accurate enough to be of much value. He himself interprets his results in such a way as to be able to make the assertion that a whole series of compounds of the two metalloids is capable of existence, characterized by having melting-points lower than those of sulphur and iodine, and losing their iodine when exposed to air.

The above somewhat detailed account of the experiments and conclusions deduced from them by Sestini and Schlagdenhauffen has been given for the purpose of exposing with sufficient fullness the way in which deductions from experimental data on this subject have been made. It is apparent that they are far from being satisfactory. This is due, in a large measure, to the fact that these investigators were guided in their researches by no good theory, if, indeed, they had any at all. In the following section a sketch is given of a theory[1] intimately applying to our subject, which may be said to possess a good basis and may be used with confidence. As the experimental data by Sestini and Schlagdenhauffen are not numerous or exact enough to permit of an application of the theory a number of experiments have been made to get additional data, of which there will be mention later on (see p. 41).

Theoretical.—The above-mentioned theory enables us, from a knowledge of the temperature at which fusion of two substances takes place and the composition of the solid phase, or, in other words, from a knowledge of the solubility of one substance in another at various temperatures—to draw pretty certain conclusions as to whether chemical combination has taken place or not. Briefly stated, the theory is as follows:

When any portion of a liquid phase of matter consisting of two substances solidifies, three cases may be distinguished:

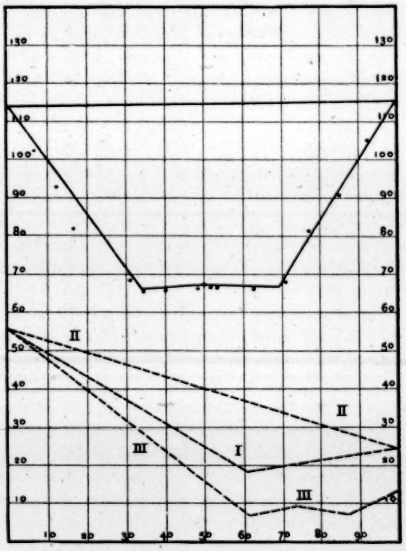
I. The two substances solidify independently.

[1] Mainly due to Le Chatelier.

II. The two substances solidify together forming isomorphous mixtures.

III. The two substances unite to form definite compounds.

These cases may be thrown into a graphical form through curves having for axis of abscissae the number of molecules (atoms) of one component contained in 100 molecules (atoms) of the mixture, and for axis of ordinates the temperatures at which fusion takes place. In Fig. 1 are drawn in dotted lines the curves characteristic of the three cases; curve I corresponding to case I; curve II to case II; and curve III to case III.



Ordinates are melting-points. Abscissae are atoms S in 100 atoms of mixture.

FIG. 1.

In the first case, the curve consists essentially of two branches cutting each other at a sharp angle, each of the branches cor-

responding to the exclusive crystallization of one of the substances. At the point of intersection of the two curves, the two substances separate out in the solid state in the same proportion as they are present in the solution, and the temperature remains constant during the change from the liquid to the solid state.

The curve representing the second case being, as it is, a straight line connecting the points of fusion of each of the component substances is quite ideal, very few, if any, mixtures presenting such a *normal* behavior; it is rare that two substances can be found which unite in all proportions to form perfectly homogeneous mixed crystals. Generally the curve is more or less convex towards the axis of abscissae, indicating non-homogeneity in the deposit, and hence a lowering of the point of solidification.

In case III ,we have to do with three definite chemical substances,—if the original substances combine in more than one proportion, more than three substances are formed and must be accounted for; for the sake of simplicity, we will assume that but one combination takes place—and it is seen that the curve is made up of four branches, each outside couple corresponding to case I. Should the compound formed be isomorphous with one of its constituents, the corresponding branches would have to be changed accordingly.

Experimental.—In order to determine to which kind of the theoretical curves, the curve drawn from data of mixtures of sulphur and iodine, and their melting-points belong, and thus to get an answer to the question whether chemical combination takes place between the two elements, experiments on the melting-points of mixtures of the two elements have been carried out, it being needless to say that such experiments are also determinations of solubility.

There are serious difficulties to be met with in the determination of the melting-points of mixtures of iodine and sulphur. At the temperature of fusion, iodine vaporizes rapidly and condenses in the cooler portion of the containing vessel; the composition of the melt is thus quite appreciably changed, and in addition, the vapors of iodine render the performance of an experiment very disagreeable. Attempts were made to

get satisfactory results with an apparatus similar to the one described by Küster,[1] but in vain. Finally the following method was adopted, which is simply the one now universally adopted for the determination of the melting-points of organic substances in the laboratory.

Mixtures of sulphur and iodine in various proportions were sealed up in small glass tubes, which were then heated in a bath of sulphuric acid to about 130°, and their melted contents well shaken together so as to form a homogeneous mixture. The tubes were then placed in a vertical position in the bath, which was allowed to cool down slowly. The lower half of the tubes, which alone was filled with the melt, was broken off, and coarsely powdered samples introduced into narrow thin glass tubes, such as used for determining points of fusion. A little above the substance these tubes were melted together so as to form a closed chamber and thus prevent the escape of iodine through volatilization. The glass tubes from which the samples had been taken, was dropped, mouth downwards, into a test-tube about half filled with a dilute solution of potassium hydrate, to absorb any escaping iodine. Generally, a bubble of air separated the solution from the solid melt, so that absorption took place slowly.

To determine the composition of the melts, the little tube, together with the caustic potash solution, was poured out into an evaporating dish, the test-tube rinsed out with a little water and the dish heated until the solid mixture melted and could be dislodged from the small tube. The action of the dissolved alkali was allowed to proceed for a couple of days at ordinary temperatures, the melt being crushed with a glass or agate pestle, so that all iodide could be absorbed. The sulphur was then filtered off into a Gooch crucible, dried at 100°–105° and weighed. The iodine was determined either gravimetrically as silver iodide or volumetrically by Volhard's method.

The temperature of fusion of the substance enclosed in the thin tubes was determined in the usual way, a thermometer divided in fifths of a degree, being used. Ordinarily, three

[1] Ueber die Erstarrungspunkte isomorpher Gemische. Zeitschrift physikal. Chemie, **8**, 578, 1891.

such tubes were prepared; with the first, the temperature was allowed to rise rapidly, and the melting-point was only approximately determined; the two subsequent determinations were made with great care. The crystals being black and yielding an opaque melt, the temperature at which fusion began was determined by watching attentively a reflecting face of a crystal, and noting as point of incipient fusion the temperature at the moment the crystal became dim; duplicate experiments gave almost identical results. The sharpness of the phenomenon of fusion varied with the proportion of the metalloids in the mixture; the degree of accuracy in the determinations may be put at less than 0.3° when the composition varied between S = 30 to 70, and less than 3° in the intervals S = 0 to 30 and S = 70 to 100. As it is in the inner interval that the decisive data are obtained, the above degree of accuracy may be reckoned sufficient.

The sulphur used in the experiments was bought as chemically pure, but, to make sure, it was crystallized a couple of times from carbon bisulphide; its melting-point was 115°. The iodine had been sublimed twice; its point of fusion was 114.1°.

The results of the determinations are given in Table I, and are represented graphically in Fig. 1 by the full-line curve. In the table, the first column gives the number of the experiment, the second the number of atoms of sulphur contained in 100 atoms of the mixture, and the third the temperature at which fusion occurs. Data marked with a star are due to Sestini (*loc. cit.*).

TABLE I.

1. No. of experiment.	2. No. atoms S in 100 atoms of mixture.	3. Temperature of fusion.	1. No. of experiment.	2. No. atoms S in 100 atoms of mixture.	3. Temperature of fusion.
1.	0.00	114.1	10.	50.00	66.2
2.	6.38	102.0	11.	51.10	66.2
3.	12.14	92.0	12.	54.51	66.0
4.	14.53	83.0	13.	63.13	66.1
5.	*21.10	75.0	14.	69.72	67.6
6.	*31.03	67.5	15.	76.33	81.0
7.	34.22	65.3	16.	84.14	88.0
8.	41.09	66.0	17.	94.21	107.0
9.	48.92	66.1	18.	100.00	115.0

Discussion of Results.—The curve from the foregoing data is entirely similar to the theoretical one, No. III. We are, therefore, justified, if the theory be correct, in admitting that the two elements have entered into true chemical combination, forming a compound containing equal numbers of atoms of both elements; furthermore, only one compound can be said to exist.

It may be worth while to consider the phenomena attendant upon the addition of sulphur to melted iodine. Suppose to melted iodine just at its point of fusion, a little sulphur be added; it enters into combination with the iodine; the sulphur iodide thus formed dissolves, and in accordance with the law that fixed dissolved substances, lower the melting-point; the system can remain in a state of fusion at a lower temperature than can the pure iodine. Let more sulphur be now added; the result is that more sulphur iodide is formed, and the point of solidification is still further lowered. Let this operation be repeated until there is more iodine in a state of combination than in a state of freedom. If now, the temperature be lowered until a solid separates out, it is quite as likely that this will be the sulphur iodide as pure iodine, that is, the system may be regarded as a solution of iodine in sulphur iodide, since it is customary to regard as solvent that component of the mixture which separates out in the operation in question. In this case the addition of more sulphur, inasmuch as it increases the amount of sulphur iodide, which is now the solvent, renders the solution more dilute; the amount of free iodine increasing continually, the melting-point of the solution rises, until, after sufficient sulphur has been added to combine with all the iodine, a compound according to definite chemical proportions remains in a state of purity.

Entirely similar phenomena would be observed, if, starting with pure melted sulphur, we should add portions of iodine. Also, it may be added that no great complication would be introduced in the above considerations, if several compounds of the two elements should be formed; it would simply be necessary to treat each of the compounds or elements with the next lower or higher compound, or element, just as in the case considered above.

III.

COMBINATION IN SOLUTIONS OF ELEMENTS.

Historical.——As mentioned on page 35, Lamers (*loc. cit.*) claims to have found that from solutions of sulphur and iodine in carbon bisulphide, a compound having a composition corresponding to the formula SI_4 crystallizes out; the solutions prepared by him had the following compositions (the amount of carbon bisulphide is not given):

I.	4 equivalents of sulphur	to	1	equivalent of iodine.
II.	2 "	"	1	"	"
III.	1 equivalent	"	1	"	"
IV.	1 "	"	3	equivalents	"
V.	1 "	"	5	"	"

Analyses of the crystalline deposits gave these results:

Crystals from solution.	I.	II.	III.	IV.	V.
I.	96.2	95.6	95.8	95.9	96.3
S.	3.8	4.4	4.2	4.1	3.7
	100.0	100.0	100.0	100.0	100.0

Although the proportions of the two metalloids in the solution vary considerably the composition of the crystals is approximately the same, and corresponds to a compound containing six times as many atoms of iodine as of sulphur, which requires 96 per cent. iodine, and 4 per cent. sulphur.

In order to obtain this "sulphur hexaiodide," Lamers states that it was necessary to conduct the evaporation very slowly at low temperatures; if the evaporation took place rapidly at higher temperatures (summer heat), crystals containing less sulphur were obtained.

It seems contrary to our received notions that such slight changes of outward conditions should have such a considerable influence upon the composition of the product. It is doubtful whether much confidence can be placed in Lamers' observations. Rath found the specimens of the "hexaiodide" submitted to him for crystallographic examination to be more of the nature of isomorphous mixtures than well-defined compounds. As a matter of fact, we find in Schlagdenhauffen's paper statements to the effect that Lamers' "hexaiodide" is not the only compound formed in solutions of sulphur and

iodine in carbon bisulphide, but that it is merely a "member of the same family of compounds which are all soluble after their fusion in carbon bisulphide." Schlagdenhauffen does not, however, communicate any numerical results, contenting himself with general statements. No other work seems to have been done on this phase of our subject, if we except the thermo-chemical investigation by Ogier (*loc. cit.*).

Experiments on the Crystallization of Carbon Bisulphide Solutions of Iodine and Sulphur.—To get data that may aid in judging of the value of Lamers' and Schlagdenhauffen's observations, I have carried out some experiments on the crystallization of the two elements from carbon bisulphide solution. Concentrated solutions containing the metalloids in the proportion of one atom of sulphur to one atom of iodine were allowed to evaporate very slowly at temperatures varying from 10° to 15°. In a little over 24 hours, crystals began to separate out around the sides of the crystallizing dish at the point of juncture of the liquid and the glass, some samples of which were removed and analyzed,[1] a composition corresponding to the formula $S_n I_n$ (n being any whole number) being found. In a day or so, new crystals which had been deposited were taken and analyzed, identical results being obtained. And, finally, when all the solvent had evaporated, some crystals in the bottom of the dish were found to have the same composition. It seems evident then that under these circumstances, a compound of iodine and sulphur is formed containing an equal number of molecules of each of the elements. How Lamers obtained the results given in his paper from solutions of the same concentration as the one which I examined it is impossible to say, especially since he lays such emphasis upon the conditions according to which the crystallization must take place, and apparently worked with considerable care. In this connection it may be added that his experiments and observations on the influence of a change of temperature upon the product obtained also seem to need revision. So far as Lamers' work is concerned, it is very probable that his "hexaiodide of sulphur" is not a definite chemical compound, although it can not be with certainty affirmed that such a combination of atoms is incapable of existence.

[1] The analysis was carried out in the same way as described for melts of the two elements on page 42.

Experiments on the Changes of the Boiling-Point of Carbon Bisulphide Caused by the Addition of Iodine and Sulphur.—If to a solution of sulphur in carbon bisulphide, iodine be added, the latter will bring about practically the same lowering of the vapor tension or raising of the boiling-point as it would, were the sulphur not present, provided that no combination between the two metalloids take place. If, however, combination occurs, the lowering of the vapor tension or the raising of the boiling-point will be less in the proportion that the iodine has combined with the sulphur. Here, then, we have a means of judging whether chemical union takes place between the two elements in solution.

A number of determinations on the raising of the points of ebullition of solutions of iodine and sulphur in carbon bisulphide have been made with a view of getting some exact data on the subject; the apparatus employed was the well-known Beckmann's ebullioscope, with the modifications recommended by Linebarger.[1] As a necessary preliminary to such determinations, the elevation of the boiling-points of solutions of iodine and of sulphur alone must be determined. Happily, such determinations have been very carefully made by Beckmann[2] for iodine and sulphur, and by Helff.[3] For convenience of reference their results are reproduced here in abridged form in Tables II and III.

TABLE II.

Beckmann's Experiments with Iodine.

No. of experiment.	Grams iodine in 100 grams CS_2.	Boiling-point elevation.	Molecular mass of iodine.
1.	1.268	0.120°	251
2.	2.910	0.270	256
3.	2.964	0.265	266
4.	6.03	0.521	275
5.	6.08	0.550	263
6.	8.97	0.777	274
7.	12.98	....	283

[1] Some Modifications of Beckmann's Ebullioscopic Apparatus. Chem. News, **69**, 279, 1894.

[2] Ueber die Molekulargrösse des Jods, Phosphors und Schwefels in Lösungen. Zeitschrift physikal. Chemie, **5**, 76, 1890.

[3] Molekulargewichtsbestimmungen der Verbindungen von Phosphor mit Schwefel und Schmelzpunkte von Gemengen beider Elemente. Zeitschrift physikal. Chemie, **12**, 196, 1893.

TABLE III.

Beckmann's and Helff's Experiments with Sulphur.

No. of experiment.	Grams sulphur in 100 grams CS_2.	Boiling-point elevation.	Molecular mass of sulphur.	Name of experimentor. (B, Beckmann; H, Helff.)
1.	1.17	0.107°	259	H
2.	1.572	0.151	247	B
3.	2.72	0.243	265	H
4.	2.895	0.276	249	B
5.	3.153	0.294	255	B
6.	4.033	0.355	270	B
7.	5.24	0.455	273	H
8.	6.14	0.540	270	B
9.	5.98	0.516	275	B
10.	7.70	0.655	279	H
11.	9.04	0.770	279	B
12.	9.32	0.761	290	H
13.	12.08	0.985	294	H
14.	14.09	1.083	308	H
15.	15.13	1.210	297	B
16.	16.23	1.264	304	H
17.	21.00	1.590	314	B
18.	22.00	1.597	326	H
19.	27.82	1.920	343	H

These tables show that there is an ever-increasing complexity in the molecules of both sulphur and iodine as the concentration becomes greater. In the case of iodine, values of the molecular masses give an average of about 254, which corresponds to the molecular formula I_2. In the case of sulphur, however, it is apparent that, while in the most dilute solutions the molecular mass is about 256, corresponding to the formula S_8, in the most concentrated solutions, the molecular mass has increased to about 320, and the molecular formula must be S_{10}. This changeability in the size of the molecule introduces considerable confusion, yet it may be possible to get some light upon the subject under investigation. In the following table are given the results of my determinations on the boiling-points of solutions of mixtures of iodine and sulphur in carbon bisulphide.

TABLE IV.

Iodine and Sulphur in Carbon Bisulphide.

MOLECULAR ELEVATION FOR 100 GRAMS $CS_2 = 23.7°$.

Grams of solvent.	Grams substance.	Elevation of boiling-point.	Parts substance in 100 parts solvent.	Molecular masses.
32.03	1.1641	0.348°	3.64	248
	IODINE CALCULATED IN CASE OF COMBINATION.			
32.03	2.7240	0.778°	8.51	260
"	4.4043	1.214	13.75	269
"	7.4890	1.943	23.41	286
"	10.2123	2.449	31.90	309
"	11.6520	2.793	36.41	313
"	12.4516	2.940	38.90	315
	CALCULATED FOR IODINE.			
32.03	1.5600	0.430°	4.87	273
"	3.2402	0.866	10.12	277
"	6.3249	1.594	19.76	293
"	9.0482	2.151	28.27	310
"	10.2875	2.460	33.08	318

The molecular masses calculated in either way are without any essential difference. If we assume that the molecule of sulphur in moderately concentrated solutions, is made up of eight atoms ($S_8 = 256$), and that of iodine in the same conditions consists of two atoms ($I_2 = 254$) it is seen that the values of the molecular masses in the last table correspond well to those in the two preceding ones; and as the concentration increases, the molecular masses become greater. This behavior may be interpreted in two ways: either there is no combination and the increase in molecular size is to be attributed to an ever-increasing complexity in the molecules of the elements, or there is a partial combination of the two metalloids which augments with the concentration.[1] It is not easy to decide which of these two proposed interpretations is the more correct; indeed, it is probable that increase of size in the molecules of the elements, as well as chemical combination, take place at the same time. A circumstance which warns us not to draw conclusions except with the greatest

[1] The molecular mass of a compound represented by the formula S_8I_2 is 318, a number identical with that experimentally found in the most concentrated solutions.

circumspection, is that, in concentrated solutions, the ebullioscopic method is not entirely reliable.

We may, by other experimental means, get some light upon the subject of the chemical combination of sulphur and iodine dissolved in carbon bisulphide. In case of combination, heat changes must occur when solutions of the two metalloids are mixed; and in this connection the thermochemical research by Ogier (*loc. cit.*) may be discussed, and better cannot be done than to quote his own words: "*Iodure de soufre.*—L'iodure de soufre solide S_2I" (in atomic notation S_2I_2) "est formé à partir des éléments avec un effet thermique très sensiblement nul, ainsi qu'il résulte des experiences suivantes. D'une part, j'ai mélangé des solutions d'iode et de soufre dans le sulfure de carbone, et je n'ai observé aucun dégagement de chaleur. D'autre part, la dissolution du produit tout formé.

$$S_2I + 130^{eq}CS_2 \text{ absorbe} \ldots\ldots -2.^{cal}8.$$

Or ce nombre est précisément egal à la somme des chaleurs de dissolution de l'iode et du soufre dans le sulfure de carbone, ... Le composé avait d'ailleurs les caractère d'un corps defiué, il serait donc formé avec un dégagement de chaleur très voisin de zéro....."

Ogier does not indicate the concentrations of the solutions of sulphur and iodine which he mixed, so that from his statements only the conclusion that in dilute solutions there is no combination between the two elements is legitimate. It would be important to make some experiments on stronger solutions to see if the same conclusion holds good for them also. Unhappily no thermo-chemical apparatus is at my disposal.

If a compound of sulphur and iodine is formed in the solution, it is evident that its molecular mass is in the vicinity of 300 to 320. Now the molecular mass of a compound corresponding to the formula S_2I_2 is 318; it is, perhaps, justifiable to take this formula which from its analogy to the formula of sulphur chloride S_2Cl_2 might almost be expected, as the formula of the possibly formed compound of the two elements. As a compound corresponding to this formula was found to

be the only one obtainable by simultaneous fusion of the two elementary substances, it is probable that it is the only one formed in solution also. It can not be admitted that molecules of the formula SI were present in the solution in any considerable amount, the molecular mass of such a compound being too small; nor is it possible that a "hexaiodide of sulphur" was formed, as its molecular mass is too large; in either case, the ebullioscope furnishes sufficiently accurate indications as to its impossibility.

IV.

COMBINATION BY DOUBLE DECOMPOSITION.

Historical.—Guthrie (*loc. cit.*) states that when sulphur chloride and ethyl iodide are mixed together at ordinary temperatures, no heat is evolved, nor is there any other evidence that chemical action takes place. After sealing up in a glass tube one molecule of sulphur chloride and a little more than one molecule of ethyl iodide, and allowing the mixture to stand for twelve hours, he found on opening the tube that ethyl chloride escaped, and "magnificent" crystals were deposited, the analysis of which showed them to contain one atom of sulphur to one atom of iodine. Guthrie remarks that methyl and amyl iodides are susceptible of similar reactions, but "for obvious reasons the ethyl compound is preferred."

Schlagdenhauffen (*loc. cit.*), in continuation of Guthrie's work, studied the action of some inorganic iodides upon the sulphur chlorides, finding that if the iodide of ammonium and of potassium were sealed up with some sulphur chloride in the proportions necessary for the production of the sulphur iodide described by Guthrie, and, if the mixture be heated on a water-bath, the liquid rapidly assumes a dark violet color, due to the formation of sulphur iodide which stays in solution. After the mixture has been heated for several hours the decomposition is complete, and by repeated washings with carbon bisulphide, the chloride of ammonium and of potassium can be obtained white and pure, while through evaporation of the carbon-bisulphide solution, a crystalline

residue remains, melting at 92° to 94°[1]. The iodide of mercury and of lead also yield the sulphur iodide when heated to the temperature of boiling water in sealed tubes with sulphur chloride. In studying the reaction of iodoform on sulphur chloride, Schlagdenhauffen ascertained that the sulphur iodide was also obtained.

In the experiments mentioned in the preceding lines, no particular examination of the product of the reaction seems to have been made. Guthrie, it is true, analyzed it, but is it not possible that the analyzed substance was merely an isomorphous mixture of the two elements in proportions which happened to be atomic? Is it not plausible that the products of the reaction are ethyl chloride, together with sulphur and iodine in a state of freedom and not in combination? From the nature of the reaction and the proportions of the reacting substances, it is necessary that the two elements be in about the same proportions, whether they are free or combined. Schlagdenhauffen paid but little attention to the product obtained in the double decompositions effected by him, and the melting-point which he gives, 92° to 94°, seems to indicate that the product, if it be S_2I_2, which has a melting-point 66.2°, is quite impure.

Experimental.—I have carried out a number of experiments on the reactions between sulphur chloride and some organic iodides in order to gain more precise knowledge of the nature of the reaction and its product. The mode of operation was the following: A large test-tube of rather thicker glass than the ordinary was heated in a blowpipe flame at about a third of its length up from the closed end, and drawn out into a slender tube three to four inches long. Another constriction was made in the middle of the open part of the tube. When a mixture of an organic iodide and of sulphur chloride is poured into such a tube it occupies the lower chamber, and the tube is sealed at the upper constriction. After the reaction has taken place, and crystals have separated out from the liquid,

[1] Schlagdenhauffen gives as melting-points of the sulphur and iodine used by him 107° and 112°, respectively. This seems to indicate that he worked with quite impure material; hence, the observations and results obtained by him may have a certain qualitative value, but as quantitative data but little reliance can be placed in them.

the tube is inverted so that the mother-liquor may drain off from the solid mass without its being necessary to open the tube; in this way all action of the air and its moisture is avoided.

Reaction between Sulphur Chloride and Ethyl Iodide.—A mixture of one molecule of sulphur chloride[1] with considerably more than one molecule of ethyl iodide[2] was filled into three tubes of the same size and shape as described above, and sealed. One of the tubes was placed where it was exposed to direct sunlight for three to four hours a day, while the other two were covered with black paper and set in a dark closet. For the sake of brevity let us designate the first tube by A, the second by B, and the third by C.

On the second day of exposure, the solution in A had turned reddish brown, and an abundant crop of crystals had separated out. The tube was inverted so that the mother-liquor could drain off; two kinds of crystals were distinguishable in the mass,—slender needles seemingly transparent, and black, ill-defined, rhombic tablets.

The contents of B and C showed no change save a very slight darkening in color after standing for three days in darkness. The tube B was then heated to 99° while exposed to diffuse daylight, for half an hour. The liquid turned black and, after standing over night in a dark closet, a fine crop of crystals was deposited, in which were distinguishable two forms similar to those found in A, although here the interlaced, needle-like, transparent crystals were present in greater number. The contents of the tube C, which were carefully shielded from light, and were kept at a temperature of 15° to 20°, gradually turned darker and darker, but no separation of crystals took place until after about two weeks; in this case also, two kinds of crystals were present.

These experiments show that, as might, indeed, be expected, light and heat exercise considerable influence upon the velocity of the reaction, but not so much on the nature

[1] The sulphur chloride had been purified by repeated rectification; its boiling-point was 137.9° under 758 mm. pressure.

[2] The ethyl iodide had been fractionally distilled until a considerable quantity, boiling constantly at 72.2° under a pressure of 756 mm., was obtained. This was preserved from the decomposing action of light in a dark closet.

of the product. Additional experiments were carried out with varying proportions of the reacting liquids and under different conditions of temperature and illumination, from which it appears that raising the temperature and intensifying the illumination hastens the reaction, which in all cases yielded two sorts of crystals, although their relative quantity varied somewhat.

Samples of these crystals were subjected to analysis. The transparent ones contained almost pure sulphur, while the black ones contained iodine and sulphur in equal atomic proportions, that is, they consisted of a sulphur iodide corresponding to the formula S_nI_n. The cause or causes of the appearance of two kinds of crystals must be sought in the different solubilites of sulphur and iodine in the menstruum. In the first part of the reaction, the liquid is supersaturated with both the elements, which combine in crystallizing out to form the iodide, just as certain salts crystallize out of solution with formation of double salts. This necessitates the admission that the sulphur iodide is, to a certain degree, dissociated in solution; and the experiments on the combination of the two elements in carbon-bisulphide solution renders this admission justifiable. As soon as the solution through the deposit of the compound begins to approach saturation, or, in other words, ceases to be supersaturated with respect to the compound, iodine, owing to its greater solubility, tends to remain in solution, while the sulphur separates out alone. It was often observed that mother-liquors deposited on evaporation relatively large quantities of sulphur, a fact in corroboration of the explanation of the phenomenon proposed above. There is here an interesting and undoubtedly fruitful field for crystallographic research, many peculiarites in the modes of crystallization and forms of crystals due to the mutual influence of the three substances being observed. This is especially the case in the crystalline products obtained by the action of sulphur chloride on propyl iodide, to be described in the following paragraph.

Reaction between Sulphur Chloride and Propyl Iodide.—52 grams of normal propyl iodide[1] and 20 grams of sulphur

[1] The propyl iodide had been repeatedly fractionally distilled, and only a portion boiling at 102.5° under a pressure of 759 mm. was taken.

chloride were sealed up in a tube similar to that described on page 52, and the whole was exposed to diffuse daylight for about fourteen of the twenty-four hours. The color of the mixture darkened gradually, and on the fourth day a magnificent crop of homogeneous crystals had separated out; these had the form of rhombic tablets, often of great regularity and beauty. No sulphur crystals were present. The tube was turned upside down so as to let the mother-liquor drain off, and then that part of the tube containing the crystalline mass was sealed off. The mother-liquor, after standing for some days, deposited an additional crop of crystals, as a yellow mass (sulphur), in which were imbedded several comparatively large and well-formed octahedra. This indicates that the solubility of sulphur and iodine in this menstruum is more nearly equal than in a mixture of ethyl iodide and chloride, together with sulphur chloride. This experiment was repeated with slightly varying proportions of the reacting liquids. The results were always about the same; in one case some sulphur crystals were found in the first crop of crystals. An analysis of some of the rhombic crystals gave the accompanying results:

	Found.	Calc. for S_2I_2.
Sulphur	20.22	20.12
Iodine	79.78	79.88
	100.00	100.00

Some determinations of the molecular mass of this product in carbon bisulphide solution were made by the ebullioscopic method, the results of which are communicated on page 56, *et. seq.*

Reaction between Sulphur Chloride and Amyl Iodide.—Four grams of sulphur chloride and 10.90 grams of amyl chloride[1] were sealed up in a tube with two constrictions and set in a dark closet. In five days crystals of two sorts had separated out long yellow bars of sulphur and dark rhombs (S_2I_2?). No further experiments were made with the amyl halogen compound, as the product obtained was too heterogeneous for utilization. The difference of solubility of the two elements

[1] The amyl chloride was a product found in the collection of the laboratory, and was considerably colored by free iodine; no attempts were made to purify it beyond a single distillation.

in this menstruum is more marked than in the two previous cases.

Molecular Mass of the Product of the Reaction of Sulphur Chloride on Propyl Iodide.—The same apparatus was used as for the experiments recorded on page 49, and carbon bisulphide was the solvent. The results of the determinations are given in Table V, and are represented graphically in Fig. II.

TABLE V.

Molecular Mass of S_nI_n in Carbon-Bisulphide Solution.

a

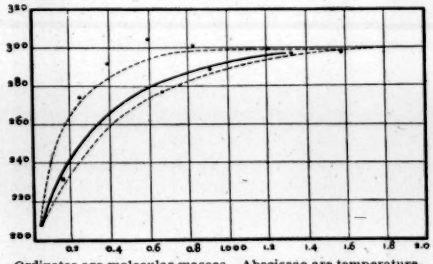
GRAMS CS_2 = 32.		BAR = 759 MM.
t	*m*	*M*
Raising of boiling-point.	Grams substance in 100 grams CS_2.	Molecular mass.
0.040°	0.35	208
0.312	3.84	288
0.860	10.25	283
1.727	21.32	293

b

GRAMS CS_2 = 38.		BAR = 760 MM.
t	*m*	*M*
0.277°	3.28	281
0.485	6.13	299
0.770	9.66	297

c

GRAMS CS_2 = 32.		BAR = 757 MM.
t	*m*	*M*
0.040°	0.35	207
0.640	7.48	277
1.442	18.00	295



Ordinates are molecular masses. Abscissae are temperature-elevations.

FIG. 2.

The data are platted in a system of co-ordinates, of which

the axis of abscissae represent elevations of boiling-points and the axis of ordinates, molecular masses. The dotted curves represent the results of the first and third series of determinations given in the table, while the heavy full line curve is intended to be a mean of both. The curves resemble completely the so-called dissociation curves; as the dilution increases, the molecular mass decreases, as might be expected from the experiments communicated on page 49. Let us consider what takes place when the sulphur iodide is dissolved in carbon bisulphide, making the assumption that in very dilute solution it is completely dissociated into its elements. The experiments of Beckmann (*loc. cit.*) and Helff (*loc. cit.*) show that the curve representing the connection between the molecular mass of iodine and sulphur and temperature elevation in solution are dissociation curves. Iodine has a molecular mass in mean equal to 254, and corresponding to the formula I_2, and sulphur may be said to have, in moderately concentrated solutions, a molecular mass equal to 256, corresponding to the formula S_8. In very dilute solution it is probable that these molecular complexes break up into simpler ones and even into the atoms. We see that in these last experiments the maximum molecular mass is a little short of 300; and it is probable that it would in more concentrated solution increase somewhat, perhaps to 318. It may be concluded here as on page 50 that the molecular formula of the sulphur iodide is S_2I_2, but that in solution it is more or less dissociated. There seems to be more affinity between the sulphur and the iodine atoms to form complex elementary molecules than to enter into combination with each other; the sulphur iodide is much of the nature of a double salt of the class referred to in my paper, "On the Existence of Double Salts in Solution."[1]

Crystalline Product Obtained from Solution of S_2I_2 in Carbon Bisulphide.—A solution of sulphur iodide (S_2I_2) which had been prepared in a molecular mass determination was poured into a crystallizing dish, covered with an inverted larger dish, and allowed to stand at temperatures varying from 15° to 20°. In a short time crystals separated out along the edges, some

[1] This Journal, **15**, 337–347, 1893.

of which were removed and analyzed. The results of the analysis were :

	Found.	Cal. for S_2I_2.
Sulphur	20.83	20.12
Iodine	79.17	79.88
	100.00	100.00

The solution was allowed to stand until all the solvent had evaporated, leaving a crystalline residue in the bottom of the dish. Some of these crystals were picked out, and their analysis gave the accompanying results :

	Found.	Calc. for S_2I_2.
Sulphur	20.17	20.12
Iodine	79.83	79.88
	100.00	100.00

These experiments show that, if it be admitted that the compound of sulphur and iodine is dissociated into molecular aggregations of the elements when in solution, combination supervenes during the act of crystallization.

V.

CONCLUSIONS.

The conclusions to be drawn from what precedes are evident. Experiments on the fusion of mixtures of iodine and sulphur, on their behavior when dissolved in carbon bisulphide, and on double decompositions of their compounds indicate that but one definite chemical compound is formed. It cannot be said, however, that other compounds of the two elements are incapable of existence ; only, the above detailed experiments give no indications of their formation. The compound formed contains equal numbers of atoms of sulphur and iodine, and its molecular formula is S_2I_2. Experiments on the boiling-point of its carbon bisulphide solutions, as well as the analogy with the chloride and bromide of sulphur (S_2Cl_2 and S_2Br_2) show this to be without doubt correct. The melting-point of the product from fusion of elements as well as that from double decomposition, was approximately the same ; *viz.*, 66.1° to 66.2°. No special crystallographic examination was

made of the products obtained in the various ways mentioned above, but all seemed to assume more or less pronouncedly the form of rhombic tablets. The compound S_2I_2 is in a very weak state of combination; it partakes more of the nature of the so-called "molecular compounds" than of that of true chemical compounds; there seems to be more tendency on the part of the iodine and sulphur atoms to form molecular aggregations than to combine with each other.

Chicago, Ill., September 17, 1894.

Contributions from the Chemical Laboratories of the Massachusetts Institute of Technology.

XII. AN INVESTIGATION OF THE TWITCHELL METHOD FOR THE DETERMINATION OF ROSIN IN SOAP.

By Thomas Evans and I. E. Beach.

When Twitchell published his method for the determination of rosin it was hoped by many that a sure means of accomplishing the desired result had been obtained. Unfortunately this was not fully justified by later experiments. Lewkowitch has shown[1] that Twitchell's process gives fairly good results, especially when the volumetric method is used, but that, while it is undoubtedly the most satisfactory process known, it is far from being exact. As Twitchell's method will be frequently referred to, a sketch of the process taken from the original article[2] is here given.

The gravimetric method is carried out as follows: Two or three grams of the mixture of fatty acids and rosin are dissolved in ten times their volume of absolute alcohol in a flask, and dry hydrochloric acid gas is passed through in a moderate stream. The flask is placed in a vessel of water to keep it cool. The hydrochloric acid is rapidly absorbed and, in about 45 minutes, the ethers separate and float upon the surface of the solution and no more hydrochloric acid is absorbed. The flask is removed from the bath and allowed to stand a half-hour longer to insure a complete combination of the alcohol and fatty acid. It is then diluted with about five

[1] J. Soc. Chem. Ind., **30**, 1893. [2] J. Anal. Appl. Chem., **5**, 379.

times its volume of water, and boiled until the acid solution is clear, the ethers with the rosin in solution floating on top. To this some naphtha is added, the whole transferred to a separatory funnel, the flask being washed out with naphtha. The acid solution is thus run off and the naphtha, which should amount to about 50 cc., washed once with water and then treated with five grams of caustic potash, which has been dissolved in five cc. of alcohol and 50 cc. of water, and agitated. The rosin is immediately saponified and the two layers separate completely. The rosin soap is then run off, treated with acid, the rosin collected in any manner desired, dried, and weighed.

The volumetric method is similar to the gravimetric in its first stages, except that the contents of the flask are washed into the separatory funnel with ether instead of naphtha, and the ether solution is thoroughly washed with water until the washings are no longer acid. Fifty cc. of previously neutralized alcohol are then added to the ether and the solution titrated with standard caustic soda.

According to Lewkowitch a loss of from 10–15 per cent. of rosin occurs when the gravimetric method is used; this he endeavored to account for but was unsuccessful.

Taking up the process with a desire to render it more exact we performed various experiments upon the same general line as Twitchell's. The samples subjected to analysis were, in most cases, prepared by mixing a known weight of rosin with a known weight of a mixture of equal parts of oleic acid and the doubly pressed fatty acids used in candle making. The rosin and fatty acids were mixed in such quantities that the resulting sample weighed about 50 grams. After mixing, the beaker containing the rosin and fatty acids was heated upon the water-bath until the contents were entirely melted, when it was cooled rapidly, being continually stirred in order to avoid separation by crystallization. It was found in each case that the rosin lost no appreciable weight by this heating, while it was always necessary to make a correction for the loss of fatty acids.

In etherizing, it was found advantageous to dissolve the sample in absolute alcohol in a 100-cc. cylinder and to place

this in a large jar containing water and a little ice. In each case two samples were etherized at the same time so as to obtain parallel results when the conditions were known to be practically the same.

In carrying out the volumetric method Twitchell's directions were followed very closely, and in the gravimetric, the recommendation of Lewkowitch, to wash the petroleum-ether layer repeatedly with a large excess of dilute caustic potash, was found greatly to facilitate separation.

The results obtained by the volumetric method when use was made of the combining weight 346 (given by Twitchell), were found to be somewhat too high, and this was at first supposed to indicate incomplete etherification of the fatty acids. It was found, however, that if the alcoholic solution, saturated with hydrochloric acid gas, was allowed to stand over night before diluting with water and boiling out the alcohol upon the water-bath, the results were appreciably lower, and that an addition of sulphuric acid to the alcohol used for dissolving the samples and standing over night as before, produced a further lowering of the percentage of rosin found. Finally, the use of methyl alcohol, instead of ethyl for etherification, appeared to give exceedingly good results as may be seen from the following table:

PERCENTAGE OF ROSIN.

	Combining weight 346.			Combining weight 328.9		
	Theoretical.	Found.	Difference.	Found.	Difference.	No.
According to Twitchell with ethyl alcohol.	40.13	42.19	+2.06	40.10	—0.03	61.
	40.13	41.74	+1.61	39.67	—0.46	76.
	40.13	42.16	+2.03	40.06	—0.07	62.
	40.13	41.69	+1.56	39.62	—0.51	63.
	40.13	41.12	+0.99	39.08	—1.05	74.
Stood 18 hours before boiling out with water.	40.13	40.31	+0.18	38.32	—1.71	54.
	40.13	40.60	+0.47	38.59	—1.54	45.
	40.13	40.77	+0.64	38.76	—1.27	52.
	40.03	39.88	—0.15	37.92	—2.11	48.
Two cc. H_2SO_4 added to alcohol; stood 41 hours.	40.13	39.53	—0.60	37.58	—2.55	34.
	40.13	39.46	—0.67	37.51	—2.62	35.
Two cc. H_2SO_4 added to alcohol, stood 21 hours..	40.13	40.03	—0.1	38.05	—2.08	36.
Two cc. H_2SO_4 added to alcohol; stood 18 hours..	40.13	40.40	+0.27	38.41	—1.72	38.

	Combining weight 346.			Combining weight 328.9		
	Theoretical.	Found.	Difference.	Found.	Difference.	No.
Two cc. H_2SO_4 added to alcohol; stood 18 hours..	40.05	40.38	+0.33	38.38	—1.67	40.
Methyl alcohol; stood 1 hour	40.05	39.93	—0.12	37.96	—2.09	5.
" " " 1½ "	40.03	39.94	—0.11	37.97	—2.08	27.
" " " 1½ "	40.03	40.04	+0.01	38.06	—1.97	11.
" " " 1½ "	40.03	39.99	—0.04	38.01	—2.02	12.
" " " 1 "	40.03	40.05	—0.02	38.07	—1.96	17.
Ethyl alcohol+2 cc. H_2SO_4; stood ½ hour.	40.13	41.59	+1.46	39.53	—0.60	
	40.13	41.89	+1.76	39.82	—0.31	

Since the rosin used in these experiments was high grade, being WG and free from foreign matter, it was at first supposed that its combining weight would be about 346, the number given by Twitchell. Repeated titration proved that this was not the case and that the combining weight was 328.9—which is very much lower than anything found by either Twitchell or Lewkowitch, the lowest combining weight found by the latter being 340.8. The last two columns in the table show the percentages of rosin actually found and their differences from the theoretical.

The foregoing analyses were selected from a series of 85 and show that methyl alcohol gives poorer results than ethyl, and that standing over night before boiling out the alcohol, causes considerable loss. These large losses upon standing and upon etherization with methyl alcohol may be attributed either to a slight etherification of the rosin or to decomposition. The fact that Twitchell and, later, we were unable to isolate any ethers of rosin makes the latter theory the more probable.

Although the time required for etherification, the volume of alcohol and the presence of sulphuric acid seemed at times to affect the results, a close study of the whole series of analyses shows that their influence was very slight.

The temperature of the bath surrounding the solution undergoing etherification, had apparently no effect upon the results, provided this temperature did not rise above 20°. If the bath is allowed to become warm, or if a very rapid stream of hydrochloric acid gas is passed through the alcoholic solution, the results are considerably lowered.

The results obtained by using ethyl alcohol and boiling out

very soon after etherizing are fairly uniform and correspond approximately with the theoretical and, while generally they are better than those reported by Lewkowitch, they differ from his quite strikingly, in that they are lower than the theoretical while his, on the whole, are higher.

Several experiments were made by weighing out the fatty acids and rosin into the graduated cylinder, dissolving in alcohol, and etherizing in the usual manner. Each of these determinations was run in check with a sample prepared in the manner first described, with the following results:

	Theoretical percentage.	Found.	Difference.
Special sample	39.87	39.36	—0.51
Ordinary sample	40.13	39.67	—0.46
Special sample	38.95	38.04	—0.91
Ordinary sample	40.13	39.08	—1.05

Since the results obtained from these specially prepared samples agree so well with those from the samples prepared in the ordinary manner, it is evident that no substantial error was introduced by the method of preparing the samples.

The rosin contained in the samples referred to was the ordinary commercial article, and, since this consists largely of resin acid anhydrides, it was deemed advisable more closely to approach the conditions of a rosin determination in a soap where the rosin would probably exist as the hydrated resin acids. With this end in view a mixture of known weights of fatty acids and rosin was saponified with alcoholic potash, the alcohol expelled by evaporation, the residual soap dissolved in water and decomposed with sulphuric acid. The fatty acids and rosin so obtained were washed free from mineral acid, dried, extracted with ether, this last expelled, and the residue used as a special sample. The results obtained from samples prepared in this way agreed very well with those prepared in the usual manner.

Finally, fearing that the fatty acids used in these samples, and those contained in an ordinary rosin soap, might differ in their behavior upon etherification, and thus tend to influence the results, several portions of the mixed oleic and solid fatty acids used in our work were dissolved in alcohol and carried through the volumetric method in the usual manner.

At the same time a sample of soap stock, such as is ordinarily used in preparing rosin soap, was obtained through the kindness of a Lawrence soap manufacturer, and the fatty acids obtained from this were treated like the mixture of oleic or solid fatty acids.

The fatty acids used in preparing the samples gave:

	1.	2.	3.	4.	Average.
Percentage unetherized acid	1.58	1.91	1.42	1.44	1.59

The fatty acids from soap stock gave:

	1.	2.	3.	4.	Average.
Percentage unetherized acid		1.70	1.72	1.88	1.77

These results, added to those previously mentioned, show conclusively that the method of preparing the samples was satisfactory and could lead to no false conclusions.

Both Twitchell and Lewkowitch carried out experiments like those just mentioned. The former found 0.97 per cent. unetherized matter in the fatty acids, which he attributed to a small amount of resin contained in the original fat. Wilson[1] in repeating Twitchell's experiments found 0.7 per cent. unetherized fat, while Lewkowitch obtained 2.28 per cent. from pure (?) stearic acid, and 5.1 per cent. from pure (?) oleic acid. The last named attributed these large percentages to incomplete etherization and seemed inclined to doubt the results of both Twitchell and Wilson. Our results, while not agreeing with those of the latter chemists, certainly approach them more closely than those of Lewkowitch.

Several attempts were made to etherize rosin alone with the following results:

Wt. of Rosin.	Rosin calculated from titration.	Difference.	Percentage loss.
2.0968 gms.	2.054	0.0428	2.00
2.4723 "	2.45	0.0223	0.90
2.035 "	2.016	0.019	0.93
2.03 "	2.016	0.014	0.69
2.115 "	2.091	0.024	1.14

As was to be expected from the analysis of mixtures, a much larger loss of rosin occurred when methyl alcohol was used in place of ethyl. Two such determinations are given:

[1] J. Soc. Chem. Ind., 10, 952.

Wt. of Rosin.	Rosin calculated from titration.	Difference.	Percentage loss.
2.0116	1.865	0.1466	7.3
2.0738	1.938	0.0358	6.6

From the tabulated results it is easily seen that when the combining weight of the rosin is known, the volumetric method gives results within the limits ordinarily required in a soap analysis. The combining weight proved to be a disturbing factor and a series of determinations was made upon various commercial samples. Those in the first column were made from a sample box of the various commercial grades of rosin, while those in the second were from rosins obtained from soap manufacturers:

No.	Grade.	Combining weight.	No.	Grade.	Combining weight.
6	WW	339.9			
7	WG	344.5	1	WG	328.9
8	N	347.5	5	N	351.4
9	M	339.8	3	M	334.5
10	K	355.6			
11	I	355.9			
12	H	354.6			
13	G	354.9			
14	F	336.8	2	F	333.5
15	E	347.9			
16	D	346.9			
17	C	350.3			

From the foregoing is seen that the combining weight of rosin varies widely in both directions from that given by Twitchell, and what is still more disappointing is that the grade, which is determined largely by the color, has little or no relation to the combining weight; so that even when the grade of rosin used is known, there is no definite basis upon which to calculate the combining weight.

Since the gravimetric method gives such untrustworthy results, the only possible way out of the difficulty seemed to be to separate the rosin gravimetrically, determine its combining weight, and use the factor so obtained in the volumetric process. Lewkowitch mentions this device as being evidently of little avail, but as he did not mention any experiments it was deemed worthy of trial.

Five grams of a mixture containing forty per cent. WG rosin (combining weight 328.9) was run through the gravimetric method and the resin acids dried at 105° C., and titra-

ted. The combining weight of these acids was found to be 328.6 in one experiment and 325.8 in another.

Four experiments with rosin N (combining weight 351.4) were then tried and negatived the results obtained with rosin WG, as the titrations gave the combining weights 329; 323.9; 331.1; 329.4. The cause of this difference was evidently due to one of two causes: either the rosin had been partially etherized or it contained unsaponifiable matter. In order to determine the cause of the discrepancy the gravimetric method was investigated more carefully.

Lewkowitch found that in carrying out this method as originally proposed by Twitchell, there was a small loss of rosin, due to incomplete saponification when shaking out the petroleum-ether layer with dilute caustic potash. This loss Lewkowitch found he could avoid by repeated extraction of the petroleum-ether layer with dilute caustic potash. He also found a more important loss in the acid wash-water first run off from the petroleum-ether solution of the products of etherification. This he recovered by extracting the wash-water with ordinary ether; but a still larger loss—which he found to be about 15 per cent.—Lewkowitch was unable to account for, although he gave as his opinion that part of the rosin was decomposed by the action of hydrochloric acid, forming acids of lower molecular weights and, possibly, condensation-products.

On reviewing his work there was evidently but one place to look for this loss; *viz.*, in the petroleum-ether layer from which the saponifiable rosin has been removed by caustic potash. Accordingly a sample of rosin N (combining weight 351.4) was run through the gravimetric method and the petroleum-ether layer, after repeated extraction with caustic potash and the complete separation of the resulting resinate solution, was evaporated to dryness. A gummy mass with a strong odor suggestive of turpentine, was thus obtained, which in one case equalled 9.71 and in another 9.54 per cent. of the original rosin. The percentages of rosin obtained from the alkaline extraction were found to be 86.78 and 86.06, thus making totals of 96.49 and 95.59 per cent. The loss in these experiments (0.07 and 0.08 gram, respectively) was probably due to experimental error.

In order to make sure that the matter obtained from the petroleum ether was not an ether, it was tested with alcoholic potash and found to be unsaponifiable. Several portions of N rosin (combining weight 351.4) were now dissolved in petroleum ether and extracted with caustic potash. The petroleum ether, on being evaporated off, left a residue of unsaponifiable matter which amounted to 8.8, 9.1, and 9 per cent., respectively, of the rosin employed. This residue looked and smelled exactly like that obtained when the rosin had been subjected to the action of hydrochloric acid. The slight excess of about 0.5 per cent. found when the rosin had been carried through the gravimetric process, may be due to decomposition, as it will be remembered that the volumetric method showed a loss of about one per cent. of rosin. A rosin and fatty-acid mixture prepared from WG rosin (combining weight 328.9) gave a loss of five per cent. of rosin by the gravimetric method, which corresponds exactly with the percentage of the unsaponifiable matter contained in this sample. Four other samples of rosin were tested for unsaponifiable matter with the following interesting results:

No.	Grade.	Percentage of unsaponifiable matter.	Combining weight of original rosin.	Calculated combining weight of sapouifiable rosin.
6	WW	7.34	339.9	315.0
1	WG	5.00	328.9	312.4
5	N	9.00	351.4	319.7
8	N	8.21	347.5	319.0
9	M	7.61	339.8	314.0
			Average,	316.0

The fact that the combining weights of the saponifiable portion of the various samples of rosin agree so well seems to bear out the statement of Maly[1] that colophony is essentially an anhydride of abietic acid.

This subject is being investigated by one of us while the other has undertaken the task of perfecting a method for the separation of the unsaponifiable rosin from the hydrocarbon oils employed as soap-fillers, etc. When this has been accomplished the Twitchell method will leave little to be desired from the soap-analyst's point of view.

[1] Jsb., 1861, 389.

A LABORATORY METHOD FOR THE PREPARATION OF POTASSIUM FERRICYANIDE.

By M. S. Walker.

The usual laboratory methods for the preparation of potassium ferricyanide by the action of chlorine or bromine water upon potassium ferrocyanide are not very satisfactory because there is generally a considerable quantity of the ferricyanides of iron formed at the same time. Several methods have been devised to overcome this difficulty, but these methods give only fair results when used by most students.

With a view to overcoming the objections to the chlorine and bromine methods, as they are employed in the laboratory, the oxidation of potassium ferrocyanide with potassium permanganate was tried and the method described below has been found very satisfactory.

Dissolve 26 grams potassium ferrocyanide in about 200 cc. cold water and add 8 cc. ordinary concentrated hydrochloric acid. Into this pour slowly a cool solution of 2 grams potassium permanganate in about 300 cc. water. The oxidation is complete if a drop added to a ferric chloride solution gives a brownish-red color but no precipitate.

Neutralize excess of acid with chalk or barium carbonate, filter, and evaporate *on the water-bath*. The first crystals will be pure. The others may contain chlorides which can be separated by fractional crystallization.

By this method beautiful crystals of pure potassium ferricyanide are obtained in the first crystallization. The crystals obtained by this method show a large development of the plane $\infty P \infty$ which rarely appears in the first crop of crystals obtained by either the chlorine or bromine methods.

This method is recommended for laboratory use because it is easy to apply, and the ferricyanide obtained is pure and shows the characteristic form of crystallization.

Johns Hopkins University,
May, 1894.

REVIEWS.

DESCRIPTIVE INORGANIC GENERAL CHEMISTRY. A text-book for Colleges. By PAUL C. FREER, M. D., Ph. D. (Munich), Professor of General Chemistry and Director of the Laboratory of General Chemistry, University of Michigan. Revised edition. Boston: Allyn & Bacon, 1894. 550 pp. Introductory price, $3.00.

This book is intended for those who "have some knowledge of the elementary principles of the science." To quote from the preface: "If an elementary course, in which every stated fact has been proved by actual experiment, precedes the work given in this book, the pupil will then be amply fitted to look at chemical phenomena from the basis of the atomic theory. It is in the hope that such a preparatory course has gone before, that I have begun this text-book with the atomic theory."

In arranging the material the author has, in the main, followed the periodic law, with such deviations as experience has shown to be called for in teaching. In general terms the work has been well done, and we have as a result an interesting, readable text-book of chemistry that is up to date. It is not an easy matter to exhibit much originality in the presentation of the fundamental facts and principles of chemistry. Probably there is no other branch of knowledge that has as many text-books as this, and it is fair to assume that most of those teachers of chemistry who have any power of presentation have tried their hands at making books. Let the work go on. Some time *the* text-book of chemistry will appear. Meanwhile we all learn something from the better new ones—sometimes, to be sure, we learn "how not to do it."

In dealing with matters of theory the author is conservative. Thus, speaking of the subject of valence, he says: "Chemists are apt to allow themselves to forget how far experiment has gone, and thus to confuse the theory and its application with the phenomena of nature. The terms 'valence' or 'bond,' used to express the means of union between atoms, may become to them material things; the lines used on paper to express the supposed manner of union of atoms may simulate real linking between existing atoms, so that at the present time, the science of chemistry is in danger of being discredited by a too dogmatic conception of the application of these methods." Occasionally, this caution is forgotten, as when, on page 4, he says: "If I subdivide any compound body,

water for instance, I can continue the operation until I arrive at the smallest individual particle thereof, a molecule." And a similar lack of caution is shown on page 442, where these words occur: "Indeed, were we acquainted with seven hundred elements, instead of seventy, these seven hundred would no more be unconnected individuals than are our present number. They, too, would fall into an arrangement, in periods and families, as the elements now do; only with such a large number of individuals, the change from family to family would not present such an abrupt transition as at present." This seems highly probable, to be sure, but more than this we are not justified in saying.

In most text-books of inorganic chemistry, the subject of constitution is still treated dogmatically, that is to say, not logically. Professor Freer cannot be accused of dogmatism. He weighs the reasons carefully and states his conclusions in such a way that the student can see the connection between the facts and the theory. One cannot help wishing that he had adopted the simple view, now commonly held, that the alums are derived from two molecules of sulphuric acid, as indicated in the formula $AlK(SO_4)_2 + 12H_2O$. This view cannot, of course, be proved to be correct, but it is in accordance with views held in regard to many other classes of compounds, and is better than that which is expressed by the formula $Al_2(SO_4)_3.K_2SO_4 + 24H_2O$. This makes alum a "double salt" in the old sense, and the author distinctly expresses his disapprobation of the "double salt" in the old sense, on page 336.

Professor Freer has made the attempt to trace "the relative influence exerted by the masses of the atoms which go to make up the molecules." What he means by this is shown by the following quotation: "The hydrogen compounds of the elements of the nitrogen family show a chemical character which differs from that found in the other two groups which have been studied, and the reason for this difference is to be found in the greater number of hydrogen atoms which are joined to one atom of the typical element contained in them. The hydrogen compounds of the halogens are acid, because one atom of each of those elements can unite with but one atom of hydrogen; the positive character of the latter, therefore, is not sufficient to counterbalance the negative properties of the halogen. The elements of the sulphur family form hydrogen compounds which are but slightly acid; for the two hydrogen atoms contained in these have twice the effect of the one in the chlorine group, while, lastly, the hydrogen compounds of the elements of the nitrogen family are either basic or neutral, for here the three hydrogen atoms entirely counterbalance the

chemical character of that of the element with which they are united." While it must be conceded that there is something in these considerations worthy of further study, this question will suggest itself: Ought not marsh gas to be more strongly basic than ammonia, if the preponderance of hydrogen is the cause of the basic properties of the latter compound?

I. R.

AN ELEMENTARY CHEMISTRY. By GEORGE RANTOUL WHITE, A. M., Instructor in Chemistry at Phillips Exeter Academy. Boston: Ginn & Co., 1894. 272 pp.

In the preface the author says that most students who take up chemistry for one, two, or three years, never intending to be chemists, waste their time. With this statement the writer of this notice is strongly inclined to agree. Mr. White has developed a somewhat novel method of approaching the study of chemistry in regard to the merits of which it is difficult to form an opinion without trying it. The first hundred pages of the book are taken up with directions for laboratory work, the character of which does not differ essentially from that given in several well-known elementary books. The chief difference between it and similar books, is seen in the lack of systematic arrangement of the subject-matter. Under Experiments, beginning page 11, after a short chapter which treats of measuring, weighing, and the wash-bottle, iron is first taken up. The pupil is directed to make certain observations on the physical properties of iron, and then to heat a weighed quantity of iron filings in a crucible, and afterwards to weigh and note the increase in weight. He is then asked: "What has caused the gain?" No answer is given in the book, and it is difficult to see what answer the pupil is to make. He can not answer without getting the necessary information either from his teacher, or some book, and this is certainly not "finding out all things for himself." Then come these words "Let us call that which has come from the air and fastened itself to the filings—oxygen, and the new dull-black substance formed—oxide of iron. Let us call oxide of iron a compound, because it is obviously compounded of two other substances. Let us call iron itself, a simple substance, because we can not make it from two or more other substances, nor can we get two or more other substances from it. What is a simple substance? What is a compound?" Can a pupil be said to have found out for himself what a compound is, and what an element is when he has performed this experiment? The second experiment involves the use of ordinary phosphorus and, in spite of the exclamation points, and the

word CAUTION three times repeated in bold-faced type, the experiment does not seem to be an appropriate one for the very beginning of a course.

The twelfth experiment is headed, "A second oxide of sulphur," and has, of course, to do with sulphur trioxide. The results of this experiment are so intangible that it can not leave a clear impression on the mind of the pupil.

Part II treats of additional experiments. These deal with bromine, iodine, fluorine, arsenic, antimony, bismuth, and the metals, tin, lead, silver, gold, platinum, and aluminum.

Part III treats of the "History and Development of the Laws and Theories of Chemistry." Experiments necessarily play a minor rôle in this part, but they are introduced wherever it seems that they will be of service. While much of that which is presented is well presented, on the whole the tone is too elevated for the beginner—at least for such beginners as have come under the observation of the writer.

I. R.

A SHORT HISTORY OF CHEMISTRY. By F. P. VENABLE, Ph. D., Professor of Chemistry in the University of North Carolina. Boston: D. C. Heath & Co., 1894. 163 pp.

The author of this little book has for some years past given his classes a short course on the history of chemistry, because from his own experience, and that of his students, he has reached the conviction, that the study of the history is one of the best aids to an intelligent comprehension of the science of chemistry. This book is based upon the course given. It is clearly written, and is interesting. One can not but admire the skill of the author that has enabled him to condense so much in so small a space, and yet to avoid squeezing the juice out of it.

I. R.